Supporting Information

C-H Bond Activation Mediated by Air-Stable $[(diimine)M^{II}(OH)]_2^{2+}$ Dimers (M = Pt, Pd)

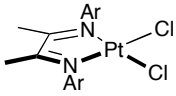
Travis J. Williams, Andrew J. M. Caffyn, Nilay Hazari, Paul F. Oblad, Jay A. Labinger,* John E. Bercaw*

I. General Methods

^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature using a Varian Inova 500, 600, or Mercury 300 spectrometer. The data are reported by chemical shift (ppm) from tetramethylsilane, multiplicity (s, singlet; d, doublet; t, triplet; m, multiplet; dd, double doublet; dt, double triplet), coupling constants (Hz), and integration. All ^{13}C NMR data were collected proton-decoupled ($^{13}C\{^1H\}$), except where specified. Mass spectra were acquired on a Finnigan LCQ ion trap or Agilent 5973 Network mass selective detector and were obtained by peak matching. All reactions were carried out under an atmosphere of nitrogen (drybox) or argon (standard Schlenk techniques) in glassware that had been oven-dried. Unless otherwise noted, all reagents were commercially obtained and, where appropriate, purified prior to use. Tris(pentafluorophenyl)borane [$B(C_6F_5)_3$] was purified by sublimation (90 °C, 0.5 Torr). 2,2,2-Trifluoroethanol-d_3 (TFE-d_3) was dried over 3 Å molecular sieves for at least 5 days and then vacuum distilled onto $B(C_6F_5)_3$. After 6 h, the TFE-d_3 was vacuum distilled and stored in a Teflon needle-valved vessel. When used in anhydrous conditions, dichloromethane-d_2 (DCM-d_2) and dichloroethane-d_4 (DCE-d_4) were prepared by vacuum transfer from a suspension of CaH_2 and filtration through a syringe filter to remove particulate residue. Anhydrous dichloromethane was prepared by sparging rigorously with nitrogen and passing through a column of activated alumina. The platinum dichloride complexes were synthesized following earlier reported procedures, as noted. TFE-d_3, DCM-d_2, DCE-d_4, $B(C_6F_5)_3$, and platinum and palladium complexes were stored in a Vacuum Atmospheres nitrogen atmosphere drybox.

II. Experimental Details for New Compounds

Dichloroplatinum Complex **6a**:[1]



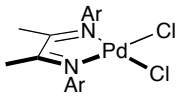
6a
Ar = 3,5-*t*Bu$_2$C$_6$H$_3$

Potassium trichloro(ethylene)platinate(II) monohydrate[2] (615 mg, 1.59 mmol) and 1,3-bis(3,5-di-*tert*-butylphenyl)-2,3-dimethyl-1,3-diaza-1,3-butadiene[3] (807 mg, 1.75

mmol) were weighed out in an oven-dried 50 mL round bottom flask with stir bar. The flask was sealed with a septum, flushed with argon, and cooled to 0 °C. Methanol (10 mL, Omnisolv™, stored over 3 Å sieves) was added and the suspension was stirred 24 hours as it was allowed to warm to room temperature. The resulting suspension was filtered over a Büchner funnel to yield a brown solid, which was washed with hexane. Excess solvent was removed under reduced pressure to give a brown solid, 1.2 g, > 95%.

^{1}H NMR (500 MHz, dichloromethane-d_2, 21 °C) δ = 7.44 (t, ^4J(H,H) = 1.7 Hz, 2H), 6.98 (d, ^4J(H,H) = 1.7 Hz, 4H), 1.79 (s, 6H), 1.37 (s, 36H). ^{13}C{^{1}H} NMR (125 MHz, dichloromethane-d_2, 21 °C) δ = 177.5 (2C), 152.0 (4C), 145.5 (2C), 122.6 (2C), 118.3 (4C), 35.6 (4C), 31.6 (12C), 21.2 (2C). FTIR (KBr) ν = 2960.7 (s), 2904.8 (m), 2868.4 (m), 2068.8 (m), 2018.3 (m), 1600.9 (m), 1473.6 (m), 1424.8 (m), 1384.7 (m), 1363.9 (m), 1334.7 (w), 1303.1 (w), 1247.4 (m), 1153.1 (m), 1007.4 (m), 881.5 (m), 830.9 (m), 704.0 (s), 606.5 (s), 563.1 (s), 461.7 (m) cm^{-1}. HRMS for $[C_{32}H_{48}Cl_2N_2Pt]^+$: calc'd 726.2845 g/mol, found 726.2813 g/mol.

Dichloroplatinum Complex **6b**:[1]



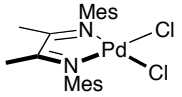
6b
Ar = 2,4,6-$Me_3C_6H_2$

In a drybox, potassium trichloro(ethylene)platinate(II) monohydrate[2] (566 mg, 1.54 mmol) was weighed out in an oven-dried 50 mL round bottom flask with stir bar. Methanol (7 mL, Omnisolv™, stored over 3 Å sieves) was added and the flask was cooled to 0 °C. 1,3-bis(2,4,6-trimethylphenyl)-2,3-dimethyl-1,3-diaza-1,3-butadiene[3] (542 mg, 1.69 mmol) was then slowly added (over 2 minutes) to the reaction mixture as a solid. The flask was sealed with a septum and allowed to warm to room temperature. The suspension was stirred 5 for hours and then filtered over a Büchner funnel to yield a brown solid. The solid was washed with Et_2O and excess solvent was removed under reduced pressure to give a brown solid, 820 mg, 90%.

This compound was insoluble in most common solvents and was only characterized by ^{1}H NMR spectroscopy. It was used in subsequent steps without further purification.

^{1}H NMR (500 MHz, dimethylsulfoxide-d_6, 21 °C) δ = 6.98 (s, 4H), 2.29 (s, 6H), 2.17 (s, 12H), 1.74 (s, 6H).

Dichloropalladium Complex **7b**:



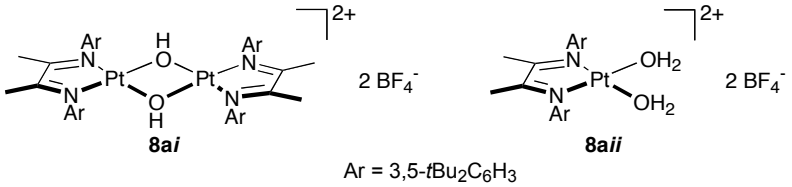
7b

Bis(benzonitrile)palladium(II) chloride (920 mg, 2.40 mmol) was dissolved in dichloromethane (8 mL) in an oven-dried 100 mL round bottom flask equipped with a stir bar. In a separate oven-dried 50 mL round bottom flask 1,3-bis-(2,4,6-trimethylphenyl)-2,3-dimethyl-1,3-diaza-1,3-butadiene[3] (769 mg, 2.40 mmol) was dissolved in dichloromethane (6 mL) and added dropwise to the palladium solution. A yellow solid precipitated out of solution immediately and the reaction mixture was left to stir for one hour. The resulting suspension was filtered over a Büchner funnel to yield a yellow solid,

which was washed with dichloromethane and diethyl ether. Excess solvent was removed under reduced pressure to give a yellow solid, 1.02 g, ~ 85%.

This compound was highly insoluble in all common solvents and was not characterized. It was used in subsequent steps without any further purification.

Platinum Hydroxide Dimer **8a*i***:[4]

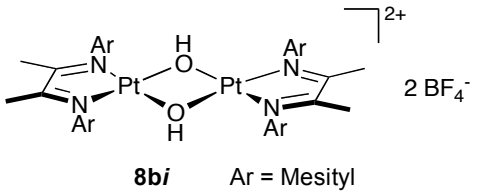


In the drybox, **6a** (545 mg, 750 μmol, prepared above) and silver tetrafluoroborate (307 mg, 1.57 mmol) were weighed out in an oven-dried 50 mL round bottom flask with a stir bar. The flask was sealed with a septum and removed from the box. To these solids were added ethanol and dichloromethane (each 10 mL, Omnisolv™) under positive argon pressure, and the suspension was stirred for 3 hours at room temperature. The resulting suspension of an off-white solid in a brown solution was filtered through a pad of celite to give a translucent brown solution, which was concentrated to dryness by rotary evaporation.[5] The resulting residue was dissolved in a refluxing solution of ca. 80 mL of ca. 2.5:1 dichloromethane:tetrahydrofuran. The solution was concentrated to ca. 20 mL and cooled to 0 °C. A portion of brown solid crystallized from the chilled solution and was collected over a Büchner funnel. The mother liquors were washed with an equal volume of water and concentrated until further crystallization commenced. The resulting solution was heated until homogenous and brown solid was crystallized as before. The combined solids were washed with hexane and solvent was removed under reduced pressure to give a yellow-orange solid, 428 mg, 75%.

8a*i*: ^{1}H NMR (500 MHz, dichloromethane-d_2, 21 °C) δ = 7.40 (t, ^{4}J(H,H) = 1.7 Hz, 4H), 7.06 (d, ^{4}J(H,H) = 1.7 Hz, 8H), 1.92 (s, 12H), 1.21 (s, 72H), -0.85 (s, 2H). ^{13}C{^{1}H} NMR (125 MHz, dichloromethane-d_2, 21 °C) δ = 182.1 (4C), 153.9 (8C), 143.9 (4C), 124.1 (4C), 117.4 (8C), 35.7 (8C), 31.6 (24C), 20.3 (4C). FTIR (KBr) ν = ~3430 (b, m), 2960.7 (s), 2906.6 (m), 2870.6 (m), 1603.1 (m), 1586.5 (m), 1473.6 (m), 1426.3 (m), 1389.5 (m), 1364.8 (m), 1305.6 (w), 1248.4 (m), 1151.5 (m), 1078.2 (s), 1061.3 (s), 884.0 (m), 710.0 (m), 552.1 (m) cm^{-1}. HRMS for $[C_{64}H_{98}N_4O_2Pt_2]^{2+}$: calc'd 1344.6974 g/mol, found 1344.7055 g/mol.

8a*ii* is observed in kinetics runs and K_{eq} measurements (vide infra): ^{1}H NMR (300 MHz, dichloroethane-d_4, 80 °C) δ = 7.62 (t, ^{4}J(H,H) = 1.5 Hz, 2H), 7.21 (d, ^{4}J(H,H) = 1.4 Hz, 4H), 2.18 (s, 6H), 1.39 (s, 36H). δ(O*H*) changes significantly with conditions.

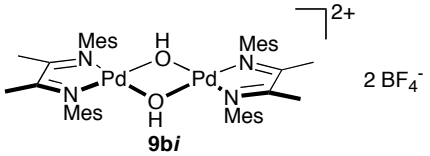
Platinum Hydroxide Dimer **8b*i***:



In the drybox, [(DAB)$PtCl_2$] (**6b**, 117 mg, 199 μmol) and silver tetrafluoroborate (80 mg, 408 μmol) were weighed out in an oven-dried 50 mL round bottom flask with a stir bar. To these solids were added ethanol and dichloromethane (each 5 mL, Omnisolv™) under positive argon pressure, and the suspension was stirred for 2 hours at room temperature. The resulting suspension was filtered through a glass frit to give a translucent orange-brown solution, which was concentrated to dryness under reduced pressure. The resulting residue was dissolved in a solution of ca. 70 mL of ca. 10:1 dichloromethane:tetrahydrofuran and the solution was cooled to 0 ºC for 7 days. Solids crystallized out of solution but dissolved as the solution warmed to room temperature. The solvent was removed under reduced pressure and the solids were dissolved in dichloromethane. The resulting solution was filtered though a glass micro-filter paper and concentrated down to ca. 2 mL. To this solution ca. 15 mL of hexanes were added and the resulting precipitate was collected over a Büchner funnel. The solids were washed with hexanes and solvent was removed under reduced pressure to give **8b*i*** as yellow solid, 101 mg, 82%.

^{1}H NMR (300 MHz, dichloromethane-d_2, 21 °C) δ = 6.94 (s, 8H), 2.34 (s, 24H), 2.21 (s, 12H), 1.98 (s, 12H), -1.02 (s, 2H). ^{13}C{^{1}H} NMR (75 MHz, dichloromethane-d_2, 21 °C) δ = 182.3 (4C), 140.3 (8C), 138.9 (4C), 130.1 (4C), 130.1 (8C), 21.5 (4C), 18.8 (4C), 17.7 (8C). HRMS for $[C_{44}H_{58}N_4O_2Pt_2]^{2+}$: calc'd 1064.386 g/mol, found 1064.383 g/mol.

Palladium Hydroxide Dimer **9b*i***:

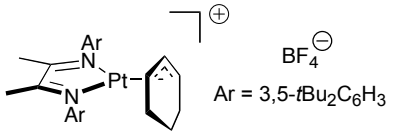


9b*i*

[(DAB)$PdCl_2$] (**7b**, 250 mg, 500 μmol, prepared above) and silver tetrafluoroborate (206 mg, 1.06 mmol) were weighed out in an oven-dried 50 mL round bottom flask with a stir bar. To these solids were added ethanol and dichloromethane (each 10 mL, Omnisolv™) under positive argon pressure, and the suspension was stirred for 3 hours at room temperature. The resulting suspension of an off-white solid in a brown solution was filtered through a pad of celite to give a translucent brown solution, which was concentrated to dryness by rotary evaporation. The resulting residue was dissolved in a solution of ca. 80 mL of ca. 2.5:1 dichloromethane: tetrahydrofuran. The solution was concentrated to ca. 20 mL and cooled to 0 ºC. A portion of yellow solid crystallized from the chilled solution and was collected over a Büchner funnel. The mother liquors were washed with an equal volume of water and concentrated until further crystallization commenced. The combined solids were washed with cold dichloromethane and solvent was removed under reduced pressure to give a yellow solid, 60 mg, 11%.

^{1}H NMR (300 MHz, dichloromethane-d_2, 21 °C) δ = 6.86 (s, 8H), 2.27 (s, 36H), 2.15 (s, 12H), -3.74 (s, 2H). ^{13}C{^{1}H} NMR (75 MHz, dichloromethane-d_2, 21 °C) δ = 183.2 (4C), 140.1 (8C), 138.6 (4C), 130.1 (4C), 129.5 (8C), 21.6 (4C), 19.4 (4C), 18.3 (8C). HRMS for $[C_{44}H_{59}N_4O_2Pd_2]^+$: calc'd for $[M\text{-}H]^+$ 887.2708 g/mol, found 887.2382 g/mol. HRMS for $[C_{44}H_{58}BF_4N_4O_2Pd_2]^+$: calc'd for $[M\text{-}BF_4]^+$ 975.2689 g/mol, found 975.2713 g/mol.

Cyclohexenylplatinum Complex **10a**:

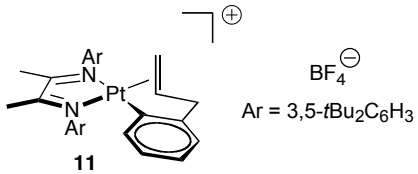


10a

Cyclohexenyl adduct **10a** was formed as described in kinetics experiments detailed in the main text and below in section III. **10a** can be isolated by concentrating a solution (in dichloromethane) to a minimal volume and adding hexane. A yellow solid forms, and can be collected over a Büchner funnel.

Data is consistent with that reported for **10a** with $[F_3BOCD_2CF_3]^-$ as the anion.[6] ^{1}H NMR (500 MHz, dichloromethane-d_2, 21 °C) δ = 7.43 (t, ^4J(H,H) = 3.4Hz, 2H), 7.01 (s, b, 4H), 5.35 (t, ^3J(H,H) = 6.4 Hz, ^1J(Pt,H) = 84 Hz, 1H), 4.14 (t, ^3J(H,H) = 6.2 Hz, ^1J(Pt,H) = 32 Hz, 2H), 2.31 (s, 6H), 2.08-2.01 (m, 2H), 1.55-1.48 (m, 4H), 1.37 (s, 36H).

Platinum-Allylbenzene Adduct **11**:

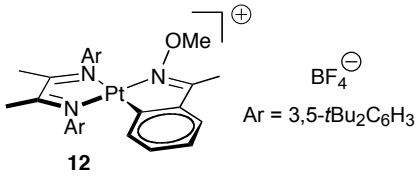


11

Allylbenzene (1.1 mg, 1.0 μL, 9.5 μmol) was added to a solution of platinum dimer dications **8a*i*/8a*ii*** (1:1.8, 5.0 mg, 3.3 μmol) in CD_2Cl_2 (1.0 mL). The solution turned orange upon standing for 3 hours at room temperature. Concentration of the solution, followed by precipitation with pentane, gave **11** as an orange powder, which can be collected over a Büchner funnel (3.0 mg, 55%).

Data is consistent with that previously reported for this known compound with $[F_3BOCD_2CF_3]^-$ as the anion.[7]

Oxime Cycloplatinate **12**:



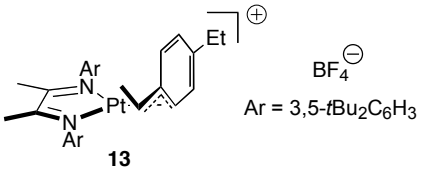
12

Platinum dimer **8a*i*** (8.2 mg, 5.4 μmol) was weighed out in a standard NMR tube on the benchtop. Dichloromethane-d_2 (700 μL) and acetophenone-*O*-methyloxime (1.2 mg, 15 μmol)[8] were added. The resulting suspension was sonicated until homogeneous and submerged (the tube was submerged up to but not including the Teflon cap) in a 80 °C oil bath for 4 days. Since the reaction was incomplete by ^{1}H NMR, another portion of oxime (4.7 mg, 56 μmol) was added. The tube was resubmerged in the 80 °C oil bath for an additional 6 days, at which point ^{1}H NMR indicated that the reaction was complete (> 95% yield). Concentration of the solution, followed by precipitation with hexane, gave **12** as a burnt orange powder, which was collected over a Büchner funnel (5.0 mg, 62%).

^{1}H NMR (500 MHz, dichloromethane-d_2, 21 °C) δ = 7.57 (t, ^4J(H,H) = 1.5 Hz, 1H), 7.48 (t, ^4J(H,H) = 1.5 Hz, 1H), 7.17 (d, ^3J(H,H) = 7.7 Hz, 1H), 7.16 (d, ^4J(H,H) =

1.8 Hz, 2H), 7.08 (d, ^4J(H,H) = 1.8 Hz, 2H), 6.95 (t, ^3J(H,H) = 7.5 Hz, 1H), 6.68 (t, ^4J(H,H) = 7.7 Hz, 1H), 5.14 (d, ^3J(H,H) = 8.1 Hz, 1H), 3.04 (s, 3H), 2.31 (s, 3H), 2.31 (s, 3H), 2.27 (s, 3H), 1.36 (s, 9H), 1.36 (s, 9H), 1.33 (s, 9H), 1.33 (s, 9H). $^{13}C\{^1H\}$ NMR (125 MHz, dichloromethane-d_2, 21 °C) δ = 183.8, 181.8, 177.5, 154.0 (2C), 152.7 (2C), 147.1, 145.9, 142.4, 141.4, 133.0, 130.5, 127.6, 125.5, 123.1, 122.4, 117.9 (2C), 117.4 (2C), 62.3, 35.7 (2C), 35.6 (2C), 31.6 (6C), 31.5 (6C), 22.2, 21.1, 12.6. FTIR (KBr) ν = 2960.7 (s), 2869.0 (m), 1600.9 (m), 1587.6 (m), 1475.5 (m), 1458.9 (m), 1437.6 (m), 1364.2 (m), 1248.3 (w), 1156.4 (m), 1083.7 (s), 1059.1 (s), 899.8 (m), 881.8 (m), 760.0 (w), 711.1 (w), 557.9 (w) cm^{-1}. HRMS for $[C_{41}H_{58}N_3OPt]^+$: calc'd 803.4228 g/mol, found 803.4223 g/mol.

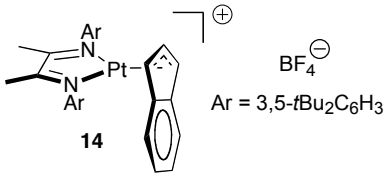
Benzylplatinum Complex **13**:



13

Platinum dimer **8a** (7.6 mg, 5.0 μmol, 2.6:1 **8a*i***:**8a*ii***) was weighed out in a J. Young NMR tube in the drybox. 2,2,2-Trifluoroethanol-d_3 (700 μL) and 1,4-diethylbenzene (8.1 μL, 6.7 mg, 50 μmol) were added, and the tube was taken out of the box and submerged (the tube was submerged up to but not including the Teflon cap) in a 90 °C oil bath for 18 hours. ^{1}H NMR analysis showed the appearance of signals matching a previously characterized sample of **13**[9] (40(5)% conversion) with $[CF_3CD_2OB(C_6F_5)_3]^-$ as the anion. Prolonged heating resulted in decomposition of the sample.

Indenylplatinum Complex **14**:



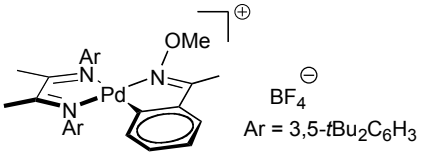
14

Platinum dimer **8a*i*** (21.0 mg, 13.8 μmol) was weighed out in a J. Young NMR tube in the drybox. Dichloromethane-d_2 (700 μL), boron trifluoride (0.44 M in 2,2,2-trifluoroethanol-d_3, 62.8 mL, 27.6 μmol) and indene (4.9 μL, 4.8 mg, 42 μmol) were added, and the tube was taken out of the box and submerged (the tube was submerged up to but not including the Teflon cap) in a 40 °C oil bath for 19 hours. Whereas the reaction was incomplete by ^{1}H NMR, the tube was taken back into the drybox and another portion of indene (4.9 μL, 4.8 mg, 42 μmol) was added. The tube was taken back out of the box and resubmerged in the 40 °C oil bath for an additional 22 hours, at which point ^{1}H NMR indicated that the reaction was complete (> 95% yield). Concentration of the solution, followed by precipitation with pentane, gave **15** as a red powder, which was collected over a Büchner funnel (20.0 mg, 84%).

^{1}H NMR (300 MHz, dichloromethane-d_2, 21 °C) δ = 7.51 (t, ^4J(H,H) = 1.7 Hz, 2H), 7.09 (dd, ^3J(H,H) = 5.6 Hz, ^4J(H,H) = 3.0 Hz, 2H), 6.91-6.83 (m, 7H), 5.02 (d, ^3J(H,H) = 2.8 Hz, ^1J(Pt,H) = 24 Hz, 2H), 5.02 (d, ^3J(H,H) = 2.8 Hz, 2H), 2.33 (s, 6H), 1.41 (s, 36H). ^{1}H NMR (500 MHz, 2,2,2-trifluoroethanol-d_3, 21 °C) δ = 7.63 (t, ^4J(H,H) =

1.7 Hz, 2H), 7.09 (dd, ^3J(H,H) = 5.6 Hz, ^4J(H,H) = 2.9 Hz, 2H), 6.90 (b, s, 4H), 6.82 (dd, ^3J(H,H) = 5.6 Hz, ^4J(H,H) = 3.2 Hz, 2H), 6.77 (t, ^3J(H,H) = 2.8 Hz, 1H), 5.02 (d, ^3J(H,H) = 2.8 Hz, 2H), 2.22 (s, 6H), 1.41 (s, 36H). $^{13}C\{^1H\}$ NMR (125 MHz, 2,2,2-trifluoroethanol-d_3, 21 °C) δ = 172.6 (s, 2C), 155.5 (s, 4C), 151.9 (s, 2C), 135.4 (s, 2C), 129.6 (dd, ^1J(C,H) = 160 Hz, ^2J(C,H) = 6 Hz, 2C), 124.6 (t, ^2J(C,H) = 6 Hz, 2C), 119.4 (d, ^1J(C,H) = 161 Hz, 2C), 116.4 (d, ^1J(C,H) = 160 Hz, 4C), 105.4 (d, ^1J(C,H) = 181 Hz, 1C), 71.80 (d, ^1J(C,H) = 177 Hz, ^1J(C,Pt) = 126 Hz, 2C), 36.63 (s, 4C), 31.91 (q, ^1J(C,H) = 130 Hz, 12C), 18.93 (q, ^1J(C,H) = 130 Hz, 2C); *J* data from a separate non-decoupled experiment. FTIR (neat) ν = 2954.7 (m), 2903.7 (w), 2866.2 (w), 1601.0 (w), 1584.1 (w), 1423.5 (w), 1384.7 (w), 1300.7 (w), 1246.5 (w), 1051.2 (s), 707.5 (w) cm^{-1}. HRMS for $[C_{41}H_{55}N_2Pt]^+$: calc'd 770.4008 g/mol, found 770.4012 g/mol.

Oxime Cyclopalladate **15a**:

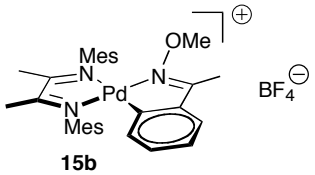


15a

Palladium dimer **9a*i*** (5.0 mg, 3.7 μmol) was weighed out in a J. Young NMR tube. Dichloromethane-d_2 (500 μL) and acetophenone-*O*-methyloxime (3.3 mg, 22 μmol)[8] were added, and the tube was submerged (the tube was submerged up to but not including the Teflon cap) in a 60 ºC oil bath for 4 hours. ^{1}H NMR spectroscopy indicated that the reaction was complete (> 95% yield). Concentration of the solution, followed by precipitation with pentane, gave **15a** as a yellow powder, which was collected over a Büchner funnel.

^{1}H NMR (500 MHz, dichloromethane-d_2, 21 °C) δ = 7.51 (s, br, 1H), 7.44 (s, br, 1H), 7. 18 (dd, ^3J(H,H) = 7.6 Hz, ^4J(H,H) = 1.5 Hz, 1H), 7.02 (s, br, 2H), 6.98 (dt, ^3J(H,H) = 7.6 Hz, ^4J(H,H) = 1.0 Hz, 1H), 6.62 (dt, ^3J(H,H) = 7.9 Hz, ^4J(H,H) = 1.6 Hz, 1H), 5.22 (dd, ^3J(H,H) = 7.9 Hz, ^4J(H,H) = 1.0 Hz, 1H), 2.99 (s, 3H), 2.40 (s, br, 3H), 2.37 (s, br, 3H), 2.26 (s, 3H), 1.34 (s, br, 18H), 1.32 (s, br, 18H). HRMS for $[C_{41}H_{58}N_3OPd]^+$: calc'd 714.3615 g/mol, found 714.3616 g/mol.

Oxime Cyclopalladate **15b**:

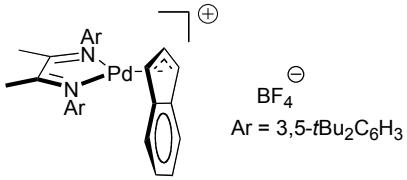


15b

Palladium dimer **9b*i*** (5.0 mg, 3.7 μmol) was weighed out in a J. Young NMR tube. Dichloromethane-d_2 (500 μL) and acetophenone-*O*-methyloxime (2.8 mg, 19 μmol)[8] were added, and the tube was submerged (the tube was submerged up to but not including the Teflon cap) in a 60 ºC oil bath for 4 hours. ^{1}H NMR spectroscopy indicated that the reaction was complete (> 95% yield). The solvent was removed under reduced pressure to give **15b** as a yellow powder which was washed with pentane.

^{1}H NMR (300 MHz, dichloromethane-d_2, 21 °C) δ = 7.21 (dd, ^3J(H,H) = 7.4 Hz, ^4J(H,H) = 1.4 Hz, 1H), 7.09 (s, 2H), 7.04 (d, ^3J(H,H) =10.1 Hz, 1H), 7.02 (s, 2H), 6.68 (m, 1H), 5.17 (d, ^3J(H,H) = 8.2 Hz, 1H), 2.83 (s, 3H), 2.41 (s, 3H), 2.35 (s, 3H), 2.30 (s, 6H), 2.25 (s, 6H), 2.23 (s, 3H), 2.15 (s, 6H). ^{13}C{^{1}H} NMR (75 MHz, dichloromethane-d_2, 21 °C) δ = 184.1, 181.7, 177.2, 152.3 (2C), 142.2 (2C), 141.7, 141.2, 139.1, 138.0, 130.3, 129.9, 129.0, 127.9, 126.6 (2C), 117.9 (2C), 115.1, 61.9, 21.2, 21.2, 21.1, 20.0 (2C), 18.4 (2C), 18.2 (2C), 12.7 (1C). HRMS for $[C_{31}H_{38}N_3OPd]^+$: calc'd for $[M]^+$ 574.2050 g/mol, found 574.2053 g/mol.

Indenylpalladium Complex **16a**:

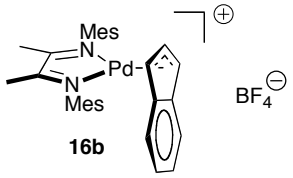


16a

Palladium dimer **9a*i*** (5.0 mg, 3.7 μmol) was weighed out in a J. Young NMR tube. Dichloromethane-d_2 (500 μL) and indene (2.0 μL, 1.8 mg, 15 μmol) were added, and the tube was submerged (the tube was submerged up to but not including the Teflon cap) in a 60 ºC oil bath for 4 hours. ^{1}H NMR spectroscopy indicated that the reaction was complete (> 95% yield). Concentration of the solution, followed by precipitation with pentane, gave **16a** as a red powder, which was collected over a Büchner funnel.

^{1}H NMR (300 MHz, dichloromethane-d_2, 21 °C) δ = 7.45 (t, ^4J(H,H) = 1.8 Hz, 2H), 7.08 (dd, ^3J(H,H) = 5.5 Hz, ^4J(H,H) = 3.2 Hz, 2H), 6.81-6.74 (m, 7H), 5.14 (d, ^3J(H,H) = 3.2 Hz, 2H), 2.33 (s, 6H), 1.41 (s, 36H). HRMS for $[C_{41}H_{55}N_2Pd]^+$: calc'd 681.3400 g/mol, found 681.3409 g/mol.

Indenylpalladium Complex **16b**:



16b

Palladium dimer **9b*i*** (5.0 mg, 3.7 μmol) was weighed out in a J. Young NMR tube. Dichloromethane-d_2 (500 μL) and indene (8.0 μL, 7.6 mg, 65 μmol) were added, and the tube was submerged (the tube was submerged up to but not including the Teflon cap) in a 60 ºC oil bath for 48 hours. ^{1}H NMR spectroscopy indicated that the reaction was complete (> 95% yield). The solvent was removed under reduced pressure to give **16b** as a red powder which was washed with pentane.

^{1}H NMR (300 MHz, dichloromethane-d_2, 21 °C) δ = 7.06 (dd, ^3J(H,H) = 5.5 Hz, ^4J(H,H) = 3.0 Hz, 2H), 7.03 (s, 4H), 6.75 (dd, ^3J(H,H) = 5.5 Hz, ^4J(H,H) = 3.0 Hz, 2H), 6.66 (t, ^3J(H,H) = 3.0 Hz, 1H), 5.10 (d, ^3J(H,H) = 3.0 Hz, 2H), 2.38 (s, 6H), 2.19 (s, 6H), 2.15 (s, br, 6H), 1.82 (s, br, 6H). ^{13}C{^{1}H} NMR (75 MHz, dichloromethane-d_2, 21 °C) δ = 172.6 (2C), 145.5 (4C), 138.2 (2C), 132.5 (2C), 130.4 (2C), 130.1 (2C), 129.2 (4C), 118.9 (2C), 111.7, 83.3 (2C), 21.2 (s, 2C), 19.1 (2C), 18.1 (2C), 17.9 (2C). HRMS for

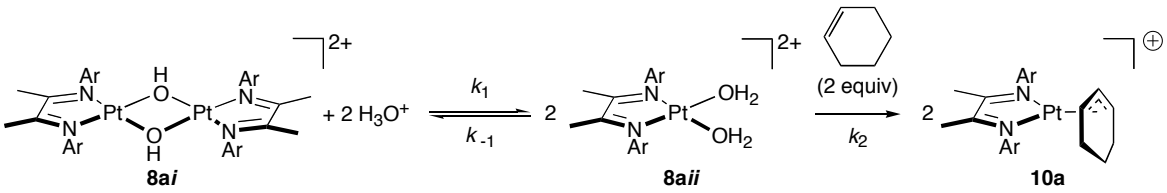
$[C_{31}H_{35}N_2Pd]^+$: calc'd 541.1852 g/mol, found 541.1835 g/mol.

Representative procedure for Cyclohexene Oxidation with mixtures of **9a*i*** and **9a*ii***, **9a*ii***, and **9b*i***:

A 1:2 mixture of **9a*i*** and **9a*ii*** (3.0 mg, 2.2 μmol) was weighed out in a J. Young NMR tube. Dichloroethane-d_4 (500 μL) and cyclohexene (16.2 mg, 197 μmol) were added, and the tube was degassed using three consecutive freeze-pump-thaw cycles. The reaction mixture was then placed under 1 atmosphere of O_2 and submerged (the tube was submerged up to but not including the Teflon cap) in a 60 ºC oil bath for 4 hours. After this time the solution was clear and a palladium mirror had formed on the glass surface. ^{1}H NMR and gas chromatography were used to determine the relative proportions of benzene, cyclohexene and cyclohexane. In cases where catalysis was performed using pure **9a*ii*** a small amount of trifluoroethanol-d_3 (75 μL) was added to assist in solubilizing the catalyst. Except in specific cases mentioned below, no extra precautions were taken to ensure that the O_2 was mixed in the solution.

III. van't Hoff and Kinetics Data

Scheme S1. Conversion of **8a** to **10a**



Preparation of samples

8a*i* (19.3 mg, 12.7 μmol) was weighed out in a 5 mL volumetric flask in the drybox, and the volume was made up with 1,2-dichloroethane-d_4. 500 μL of this solution was distributed into a screw-capped NMR tube, and each was further diluted with 200 μL DCE-d_4. Appropriate amounts of cyclohexene and/or borofluoric acid (48%, 7.65 M aqueous, at the temperatures at which these experiments were conducted all the borofluoric acid appeared to be dissolved in the organic layer, so that the solution only contained one phase) were added to give the samples described in tables below. These were used for van't Hoff analysis and [cyclohexene] dependence experiments.

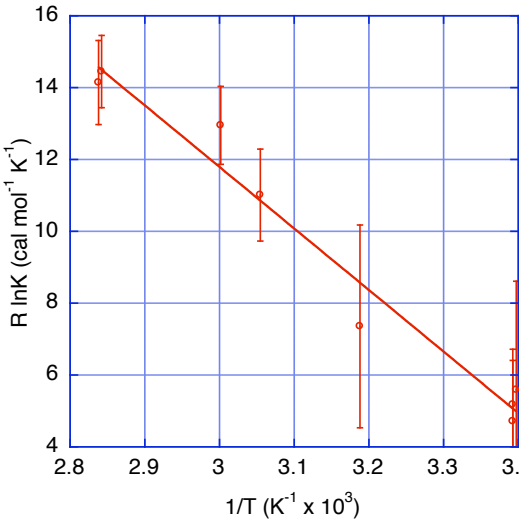
K_{eq} measurement and van't Hoff analysis

A sample of **8a*i*** and HBF_4 prepared as above was heated in a 300 MHz Varian (Mercury) NMR. K_{eq} was determined from integrations of *t*Bu peaks at the indicated temperatures (Table S1). Each sample was equilibrated at the indicated temperature until no further change was observed; this typically involved between 15 min (80 °C) and 24 hr (20 °C). The temperature was cycled twice from RT to 80 °C. Equilibrium constants at each temperature were calculated from the formula $K_{eq} = [\mathbf{8a}\textit{ii}]^2/([\mathbf{8a}\textit{i}]\bullet[HBF_4]^2)$ M^{-1}. Thermodynamic parameters obtained from the van't Hoff plot are ΔH = 17(1) kcal/mol and ΔS = 63(4) eu, R^2 = 0.971.

Table S1. K_{eq} calculations and van't Hoff plot[a]

Trial	Temp	HBF_4 (aq)	K_{eq}
1	21.2 °C	5 equiv. to Pt	1.7(25) x 10^1 M^{-1}
2	40.5 °C	5 equiv. to Pt	4.1(58) x 10^1 M^{-1}
3	60.0 °C	5 equiv. to Pt	6.8(37) x 10^2 M^{-1}
4	79.2 °C	5 equiv. to Pt	1.2(7) x 10^3 M^{-1}
5	21.6 °C	5 equiv. to Pt	1.1(9) x 10^1 M^{-1}
6	21.6 °C	5 equiv. to Pt	1.4(11) x 10^1 M^{-1}
7	54.2 °C	5 equiv. to Pt	2.6(61) x 10^2 M^{-1}
8	78.7 °C	5 equiv. to Pt	1.4(7) x 10^3 M^{-1}

[a] R^2 = 0.971



Dependence of equilibrium position on [HBF_4]

8a*i* (9.5 mg, 6.3 μmol) was weighed out in a 2 mL volumetric flask in the drybox, and the volume was made up with 1,2-dichloroethane-d_4. 600 μL of this solution was distributed into each of 3 screw-capped NMR tubes, and each was further diluted with 100 mL DCE-d_4. The tubes were removed from the drybox and 0.25 μL, 0.62 μL, and 1.23 μL borofluoric acid (48%, 7.65 M aqueous) was added to each (respectively). Each tube was equilibrated (~15 min) in the NMR probe (300 MHz) at 80(1) °C, and a ^{1}H NMR spectra was recorded.

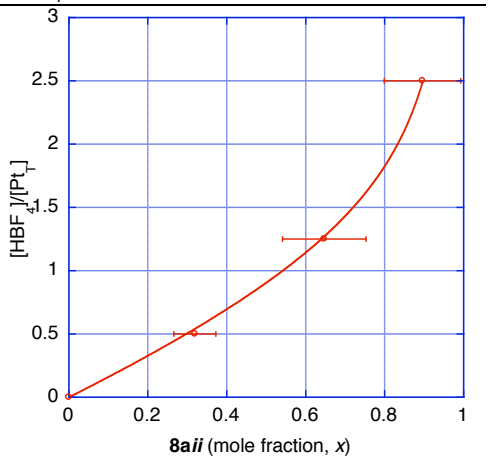
Defining [Pt] = 2[**8a*i***]+ [**8a*ii***], x = [**8a*i***]/[Pt], and μ = [HBF_4]/[Pt], we get the following relationships:

$$K_{eq} = \frac{[8aii]^2}{[8ai][HBF_4]^2} = \frac{2x^2}{[Pt](1-x)(\mu - x)^2} \qquad \mu = x + \sqrt{\left(\frac{2}{K_{eq}[Pt]}\right)\frac{x^2}{(1-x)}}$$

Data for μ vs. x are shown, along with a non-linear fit, in Table S2. The error bars arise from NMR integration over multiple peaks. The value of K_{eq} = 1.2(1) x 10^3 M^{-1} (R^2 = 0.999) agrees well with that determined above at that temperature.

Table S2. Dependence of equilibrium position on [HBF_4]

Trial	HBF_4 (μ)	Mole fraction **8a*ii*** (x)
1	1.0 equiv. to **8a*i***	31.9(53)%
2	2.5 equiv. to **8a*i***	66.5(79)%
3	5.0 equiv. to **8a*i***	92.1(87)%



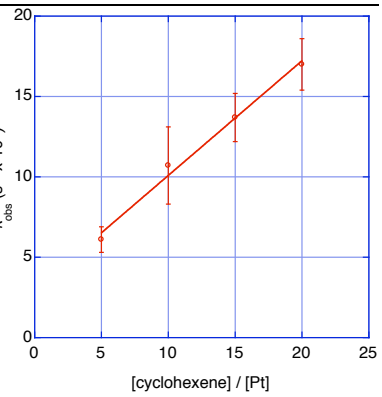
Rate dependence on cyclohexene

NMR sample tubes were prepared as described above, incubated for several hours (3-10) at room temperature, and placed in the NMR probe heated to 80 °C. By the time thermal equilibration was reached, **8a*i*** was completely converted to **8a*ii***. The conversion of **8a*ii*** to **10a** was monitored by averaging NMR intensities for each aryl C-*H* signal. k_{obs} was determined for each trial; the plot of k_{obs} vs. [cyclohexene] is shown in Table S3.

Table S3. Rate dependence on [cyclohexene][a]

Trial	[cyclohexene]	HBF_4 (aq)	$k_{2\ obs}$
1	5 equiv. to Pt	5 equiv. to Pt	6.14(90) x 10^{-4} s^{-1}
2	10 equiv. to Pt	5 equiv. to Pt	1.07(24) x 10^{-3} s^{-1}
3	15 equiv. to Pt	5 equiv. to Pt	1.37(16) x 10^{-3} s^{-1}
4	20 equiv. to Pt	5 equiv. to Pt	1.70(17) x 10^{-3} s^{-1}

a. $R^2 = 0.991$.



Rate dependence on [HBF_4]

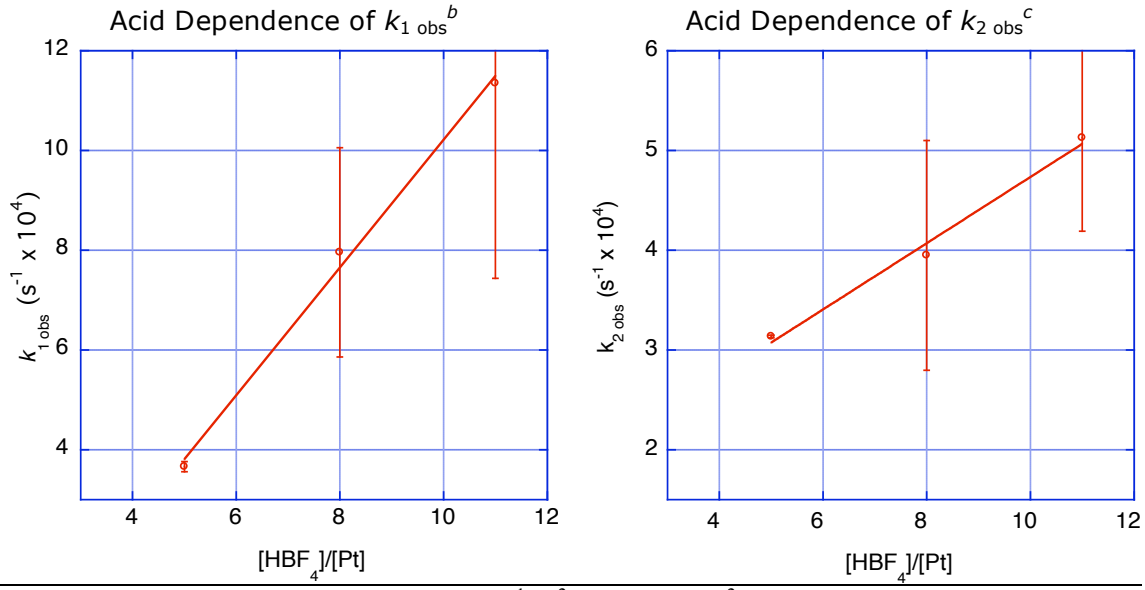
8a*i* (11.6 mg, 7.64 μmol) and cyclohexene (6.27 mg, 76.4. μmol, 7.72 μL) were mixed in a 2 mL volumetric flask in the drybox, and the volume was made up with 1,2-dichloroethane-d_4. 480 μL of this solution was distributed into each of 3 screw-capped NMR tubes, and each was further diluted with 220 μL DCE-d_4. The tubes were removed from the drybox and individually incubated in the NMR probe at 80 °C. To initiate reaction, borofluoric acid (48%, 7.65 M aqueous, as indicated) and a makeup volume of water (to make vol(HBF_4 (aq)) + vol(H_2O) = 2.6 μL = 3.7%) were injected, and kinetics data acquisition commenced *immediately*. Because of the timing of acid injection and excess water, all three species (**8a*i***, **8a*ii***, and **10a**) were observed. The ^{1}H NMR integration data was fit to the general form of the equations for the concentrations of species involved in a series of first-order reactions[10] (shown in Scheme S1), to generate values of $k_{1\ obs}$ and $k_{2\ obs}$ as shown in Table S4. The large error bars are a consequence of interference by signals due to exchangeable protons (from H_2O and HBF_4) in the NMR spectra; these obscure certain spectral markers. Since the position of the interfering peaks are concentration- and temperature-dependent, different marker peaks are masked at various points in the various runs. Concentrations were determined by averaging ^{1}H integrations of usable signals for each species, and k_{obs} values calculated by averaging rate constants obtained from the fits to the two appropriate equations.

$$[8ai] = [8ai]_o\, e^{(-k_{1obs}t)} \qquad [8aii] = \frac{k_{1obs}}{k_{2obs} - k_{1obs}}[8ai]_o\,(e^{(-k_{1obs}t)} - e^{(-k_{2obs}t)})$$

$$[10a] = [8ai]_o\left(1 + \frac{k_{2obs}}{k_{1obs} - k_{2obs}}e^{(-k_{1obs}t)} + \frac{k_{1obs}}{k_{2obs} - k_{1obs}}e^{(-k_{2obs}t)}\right)$$

Table S4. Rate dependence on $[HBF_4]$[a]

Trial	[cyclohexene]	HBF_4 (aq)	$k_{1\ obs}$	$K_{2\ obs}$	n[a]
1	10 equiv. to Pt	5 equiv. to Pt	$3.66(10) \times 10^{-4}$ s^{-1}	$3.13(1) \times 10^{-4}$ s^{-1}	2
2	10 equiv. to Pt	8 equiv. to Pt	$8.0(21) \times 10^{-4}$ s^{-1}	$3.9(12) \times 10^{-4}$ s^{-1}	2
3	10 equiv. to Pt	11 equiv. to Pt	$1.13(39) \times 10^{-3}$ s^{-1}	$5.1(9) \times 10^{-4}$ s^{-1}	4



[a] n = number of measurements of each *k*. [b] $R^2 = 0.995$. [c] $R^2 = 0.989$.

IV. Catalytic Conversion of Cyclohexene to Benzene

The results from the catalytic conversion of cyclohexene to benzene in static NMR tubes, using a mixture of **9a*i*** and **9a*ii***, pure **9a*ii***, or **9b*i***, are summarized in Table S5. These results suggest that a mixture of **9a*i*** and **9a*ii*** reacts faster than **9b*i***. It is unclear whether a mixture of **9a*i*** and **9a*ii*** reacts faster than pure **9a*ii***, as it was necessary to add some trifluoroethanol-d_3 to solubilize the catalyst when using pure samples of **9a*ii***. Also, in catalysis using pure samples of **9a*ii***, there appeared to be a long initiation period. Even after twelve hours no benzene (or cyclohexane) had formed and the oxidation/disproportionation reactions did not appear to commence until after the mixture had been heated for approximately fifteen hours. The ^{1}H NMR spectrum of the reaction mixture during the initiation period indicated that the starting Pd complex was no longer present and that several new complexes were present. At this stage it is unclear exactly what is happening in the initiation period and whether the dimer and monomer both react through the same active species.

The results from Table S5 clearly show that oxygen plays a crucial role in the reaction. In the control experiments with no O_2 present (Entry 2 and 4), the ratio of benzene to cyclohexane is 1:2, which suggests that benzene is being formed through transfer hydrogenation (disproportionation of cyclohexene to benzene and two molecules of cyclohexane). In the experiments with O_2 present, the ratio of benzene to cyclohexane is 5:4, which indicates that oxidation is taking place as well, although the transfer hydrogenation process is still occurring.

Table S5. Catalytic conversion of cyclohexene to benzene[a]

Entry	Catalyst	Temperature	Time	Atmosphere	Ratio C_6H_6:C_6H_{12}	Conversion
1	**9a*ii***	60 °C	72 h	1 atm O_2	5:4	82%
2	**9a*ii***	60 °C	72 h	1 atm Ar	1:2	25%
3	1:2 **9a*i*:9a*ii***	60 °C	4 h	1 atm O_2	5:4	44%
4	1:2 **9a*i*:9a*ii***	60 °C	4 h	1 atm Ar	1:2	38%
5	**9b*i***	110 °C	72 h	1 atm O_2	5:4	10%

[a] All reactions except for controls were performed at least twice.

A series of further reactions were performed to assess how varying the reaction conditions affected the ratio of benzene to cyclohexane. If the J. Young NMR tube was fully inverted every five seconds during heating to ensure thorough mixing of the O_2 with the solution, no cyclohexane was formed; after 72 hours, 39% of the cyclohexene had been converted to benzene. Similarly, if the reaction was performed on a larger scale in a 13 mL flask equipped with a Kontes valve (under one atmosphere of O_2), only benzene (no cyclohexane) was formed. This is presumably because in the larger vessel the surface area of the gas-liquid interface is much larger, which again allows for more efficient mixing of O_2. These results strongly imply that disproportionation is completely inhibited so long as the concentration of O_2 in solution is maintained. Conversely, after 72 hours reaction carried out in a static J. Young NMR tube, with more **9a*ii*** (9 mg, 0.012 mmol) and cyclohexene (60 μL, 0.59 mmol) but the same amount of O_2 as in Table 5, the ratio of benzene to cyclohexane was 0.75:1, which demonstrates that as the relative concentration of O_2 decreases, the amount of disproportionation increases.

To demonstrate that O_2 is consumed during the reaction, **9a*ii*** (45 mg, 0.058 mmol) and cyclohexene (120 μL, 1.18 mmol) were added to a 13 mL reaction flask

equipped with a Kontes valve which contained 5 mL of a 5:1 solution of dichloroethane-d_4 and trifluoroethane-d_3. The solution was degassed using three consecutive freeze-pump thaw cycles, and O_2 was introduced into the reaction vessel at -196 ºC from a calibrated bulb. The amount of added O_2 was established to be 1.0548 mmol by Toepler pumping the residual O_2 from the calibrated bulb. The flask was then heated for 5 days at 60 ºC, without any stirring (at 60 ºC the pressure in the flask was approximately 2 atm). After this time, the Toepler pump was used to measure the amount of O_2 left in the flask, as 0.659 mmol, indicating that 0.41 mmol of O_2 was consumed in the reaction. GC and ^{1}H NMR spectroscopy indicated that no cyclohexane had been formed in the reaction and that 36% of the cyclohexene had been converted to benzene; the stoichiometry of the oxidative dehydrogenation would require consumption of 0.42 mmol of O_2, extremely close to the experimental value.

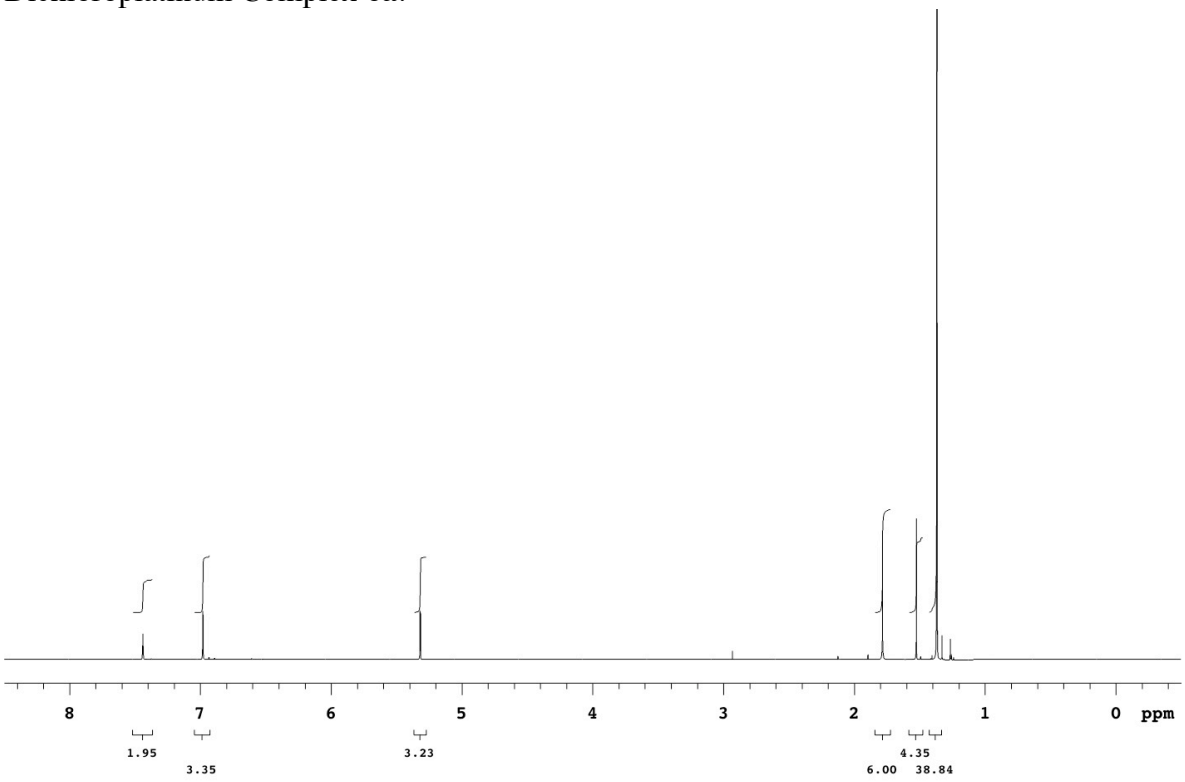
^{1}H NMR strongly indicates that water is produced in these reactions. For reactions performed in dichloroethane-d_4 without trifluoroethanol-d_3, a broad peak at δ 1.75 ppm was observed at the end of the reaction, which greatly diminished and shifted when D_2O was added to the reaction mixture. This broad resonance is presumably an average signal from the coordinated and free water present in the sample. When trifluoroethanol-d_3 is present, the (sharp) signal from residual hydroxylic proton increases during the course of the reaction. Unfortunately attempts to quantify the water generated in these reactions were not successful, because a) there is water present in the starting material and b) when the reaction is performed in the presence of trifluoroethanol-d_3, there is exchange between cyclohexene and the OD deuterium atom of trifluoroethanol-d_3.

Several tests were carried out in order to confirm that the reaction is homogeneous. First, the supernatant from a reaction between **9a*ii*** and cyclohexene was isolated by filtration. A fresh charge of cyclohexene (20 μl) was added to the supernatant and the reaction mixture was placed under 1 atm of O_2. After 6 hours at 60 ºC, 20 % conversion of cyclohexene to benzene was observed. In a related experiment, supernatant was decanted from the palladium mirror which forms from the reaction between **9a*ii*** and cyclohexene, the palladium mirror was washed with CH_2Cl_2 and then cyclohexene (20 μl) and dichloroethane-d_4 (500 μL) were added. The reaction mixture was placed under 1 atm of O_2 and heated for 6 hours at 60 ºC. After this time, no conversion of cyclohexene to benzene was observed. Furthermore, addition of a drop of elemental Hg to the reaction mixture failed to quench catalytic activity. These experiments all strongly suggest that the reaction is homogeneous.

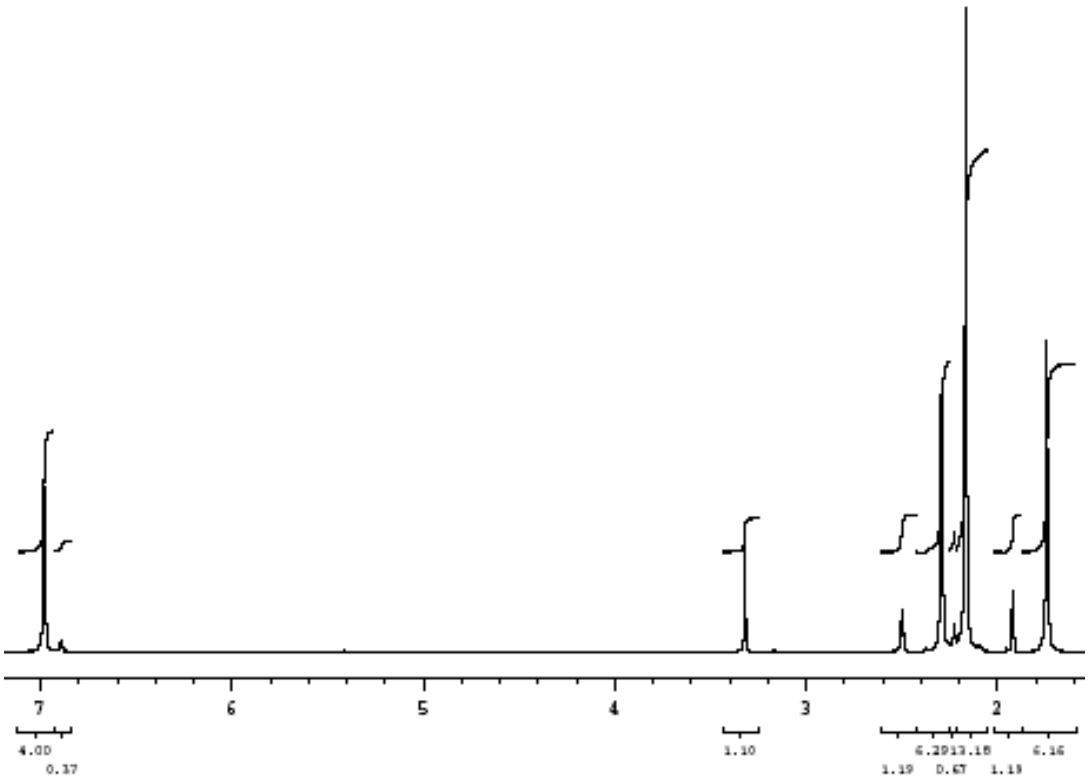
Similar experiments were performed to demonstrate that the active catalyst in the palladium(II) trifluoroacetate system reported by Trost and Metzner is heterogeneous.[11] After the initial reaction between palladium(II) trifluoroacetate (3 mg, 9 μl) and cyclohexene (18.2 μl, 0.18 mmol) in acetone-d_6, both the black solid which precipitated out of solution and the supernatant were isolated. A fresh charge of cyclohexene (15 μl) was added to the supernatant, and after 6 hours at room temperature, no conversion of cyclohexene to benzene was observed. In contrast, when a fresh charge of cyclohexene (15 μl) and acetone-d_6 were added to the black precipitate, complete conversion of cyclohexene to benzene and cyclohexane was observed in 45 minutes.

V. Selected Graphical ^{1H} Spectra for New Compounds

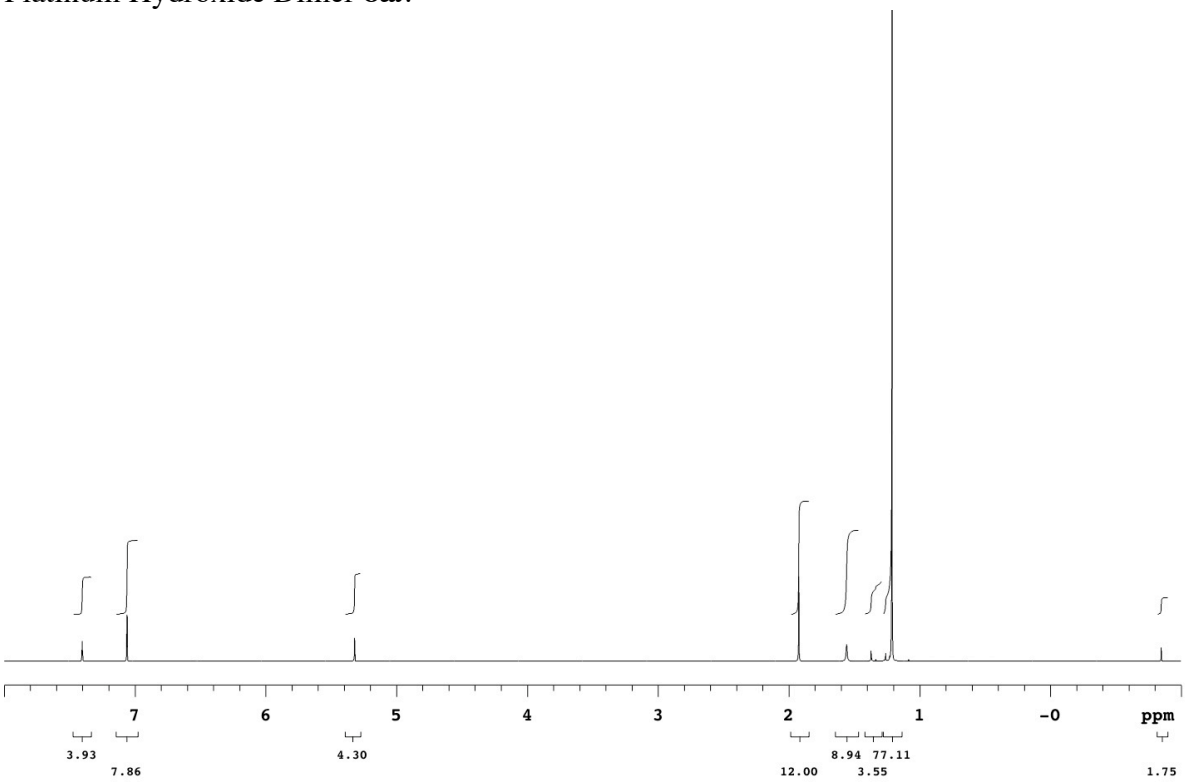
Dichloroplatinum Complex **6a**:



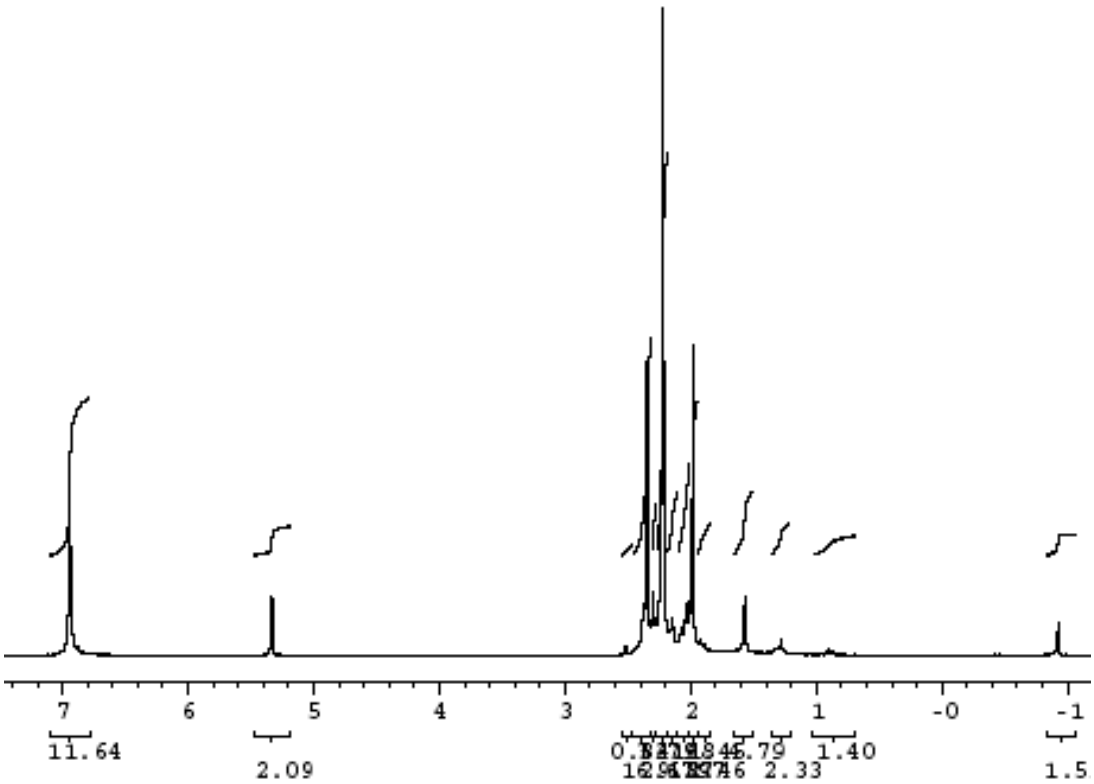
Dichloroplatinum Complex **6b**:



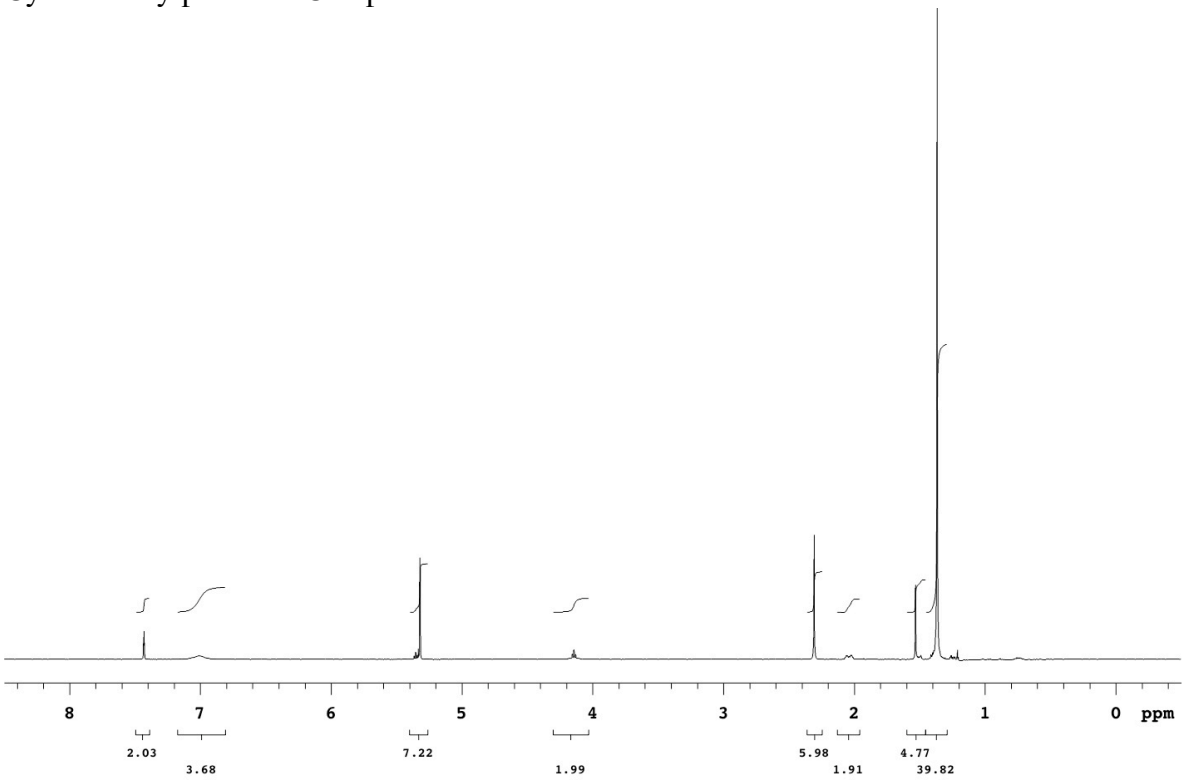
Platinum Hydroxide Dimer **8a*i***:



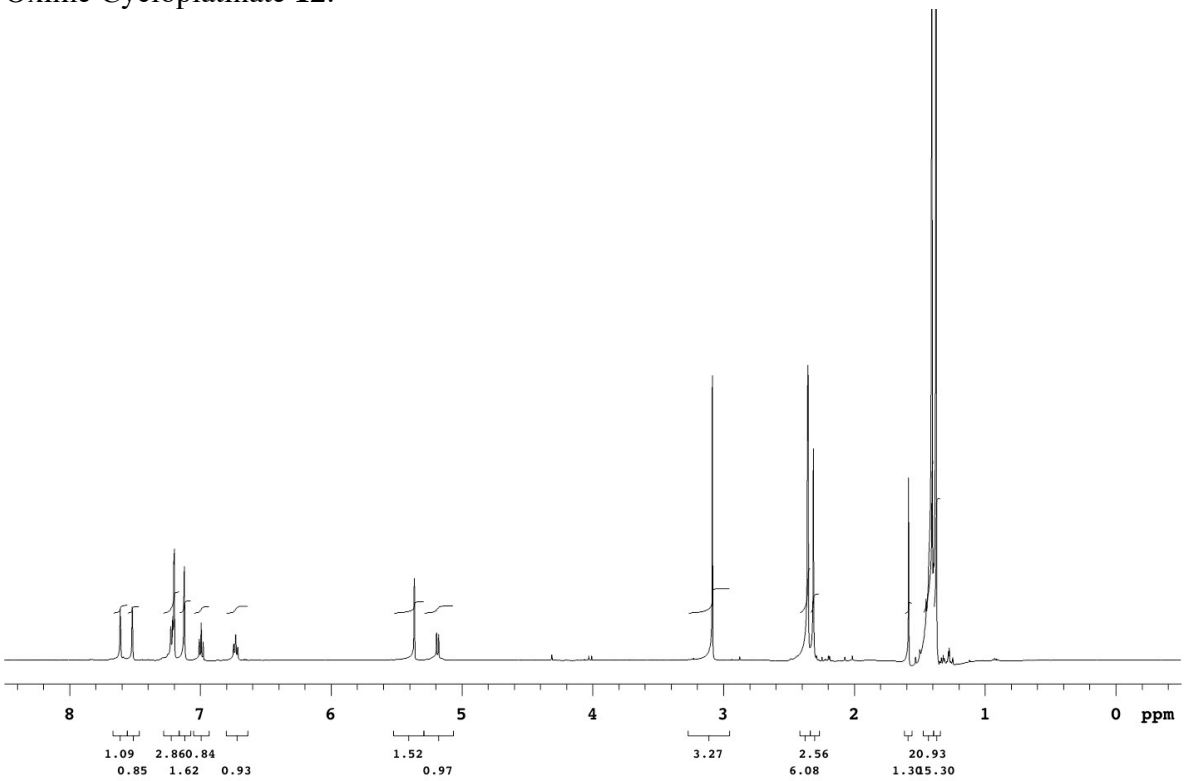
Platinum Hydroxide Dimer **8b*i***:



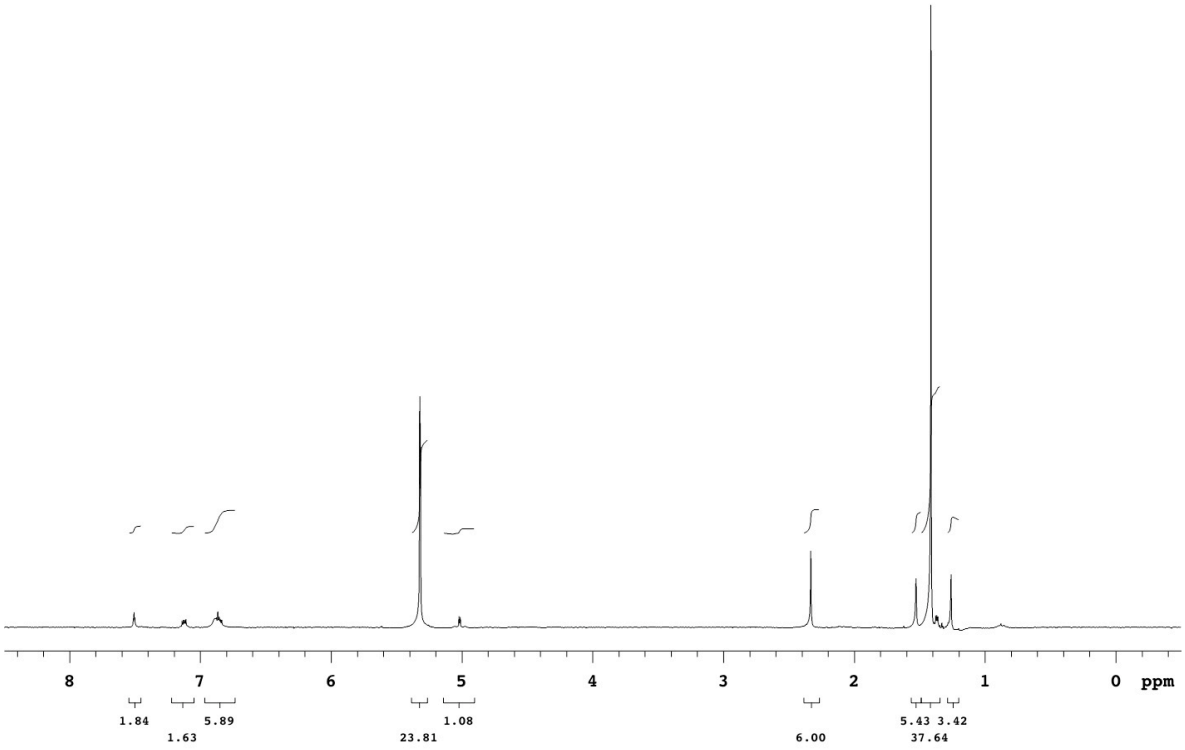
Cyclohexenylplatinum Complex **10a**:



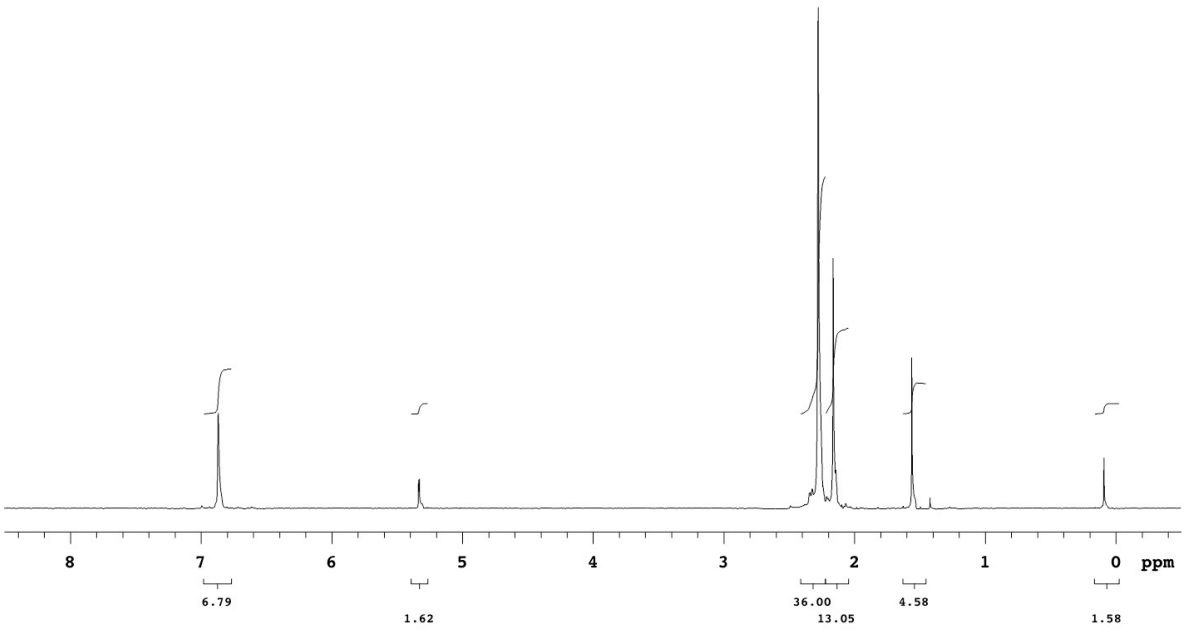
Oxime Cycloplatinate **12**:



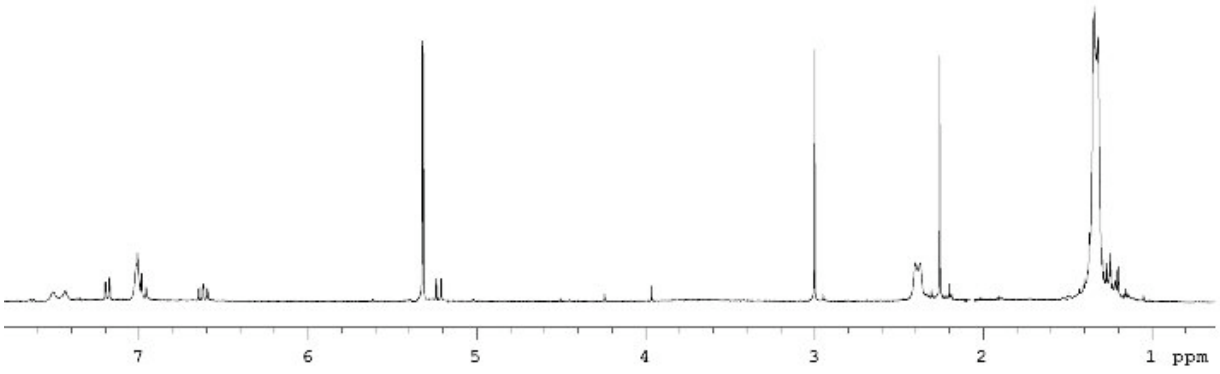
Indenylplatinum Complex **14**:



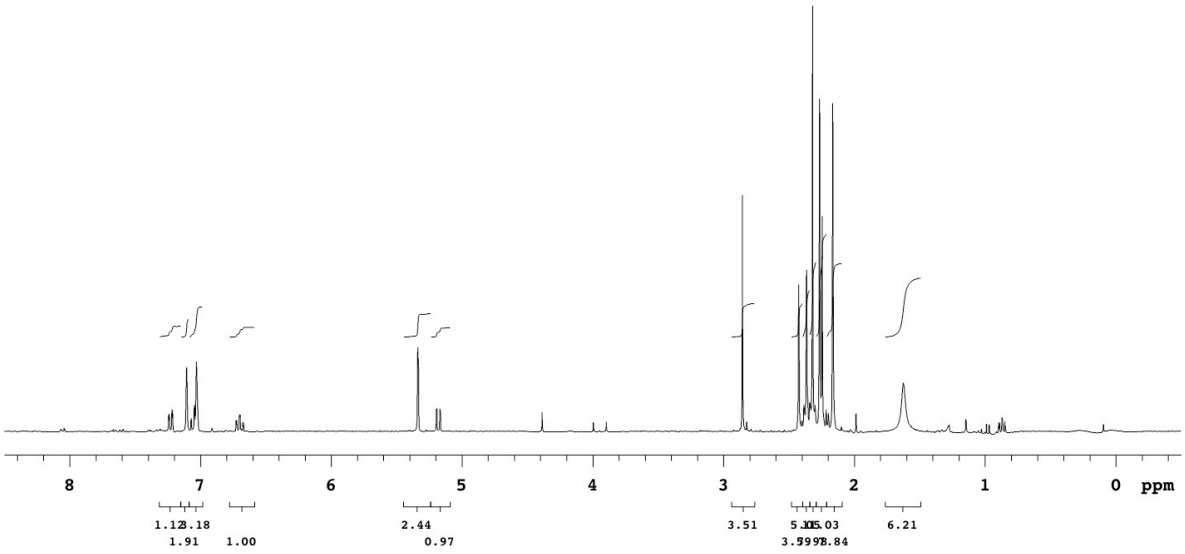
Palladium Hydroxide Dimer **9b*i***:



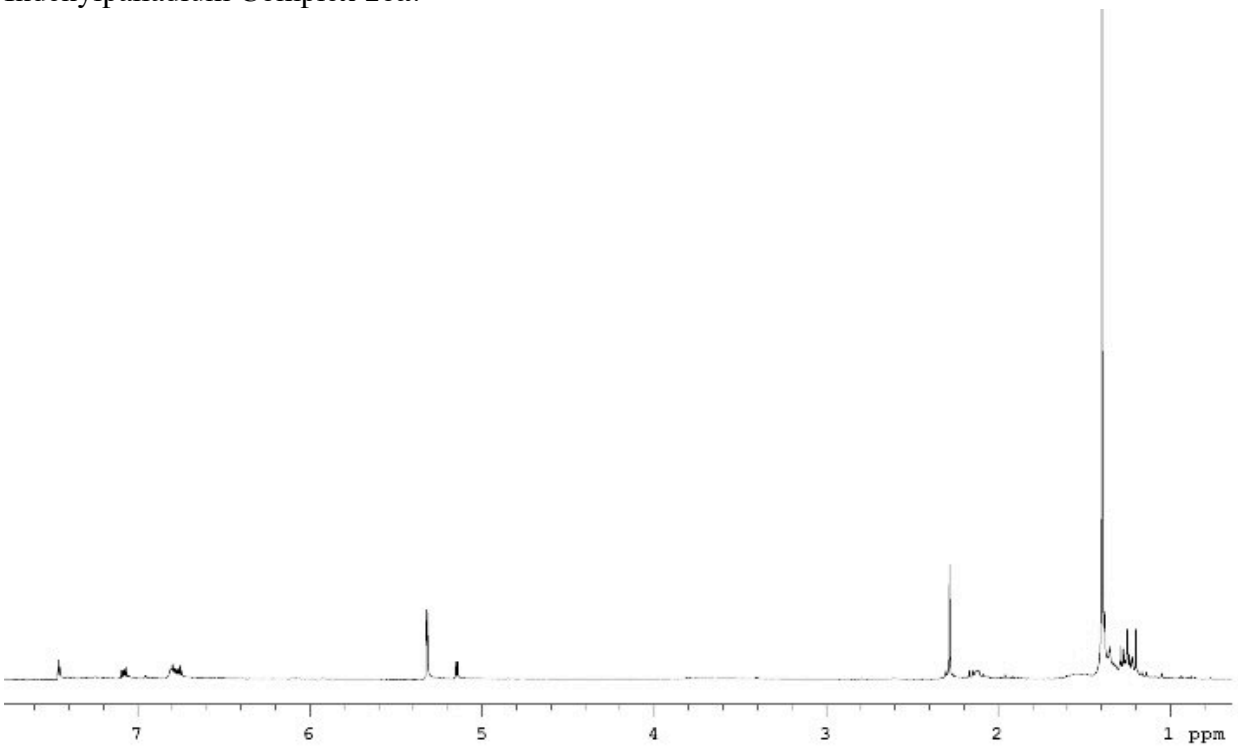
Oxime cyclopalladate **15a**:



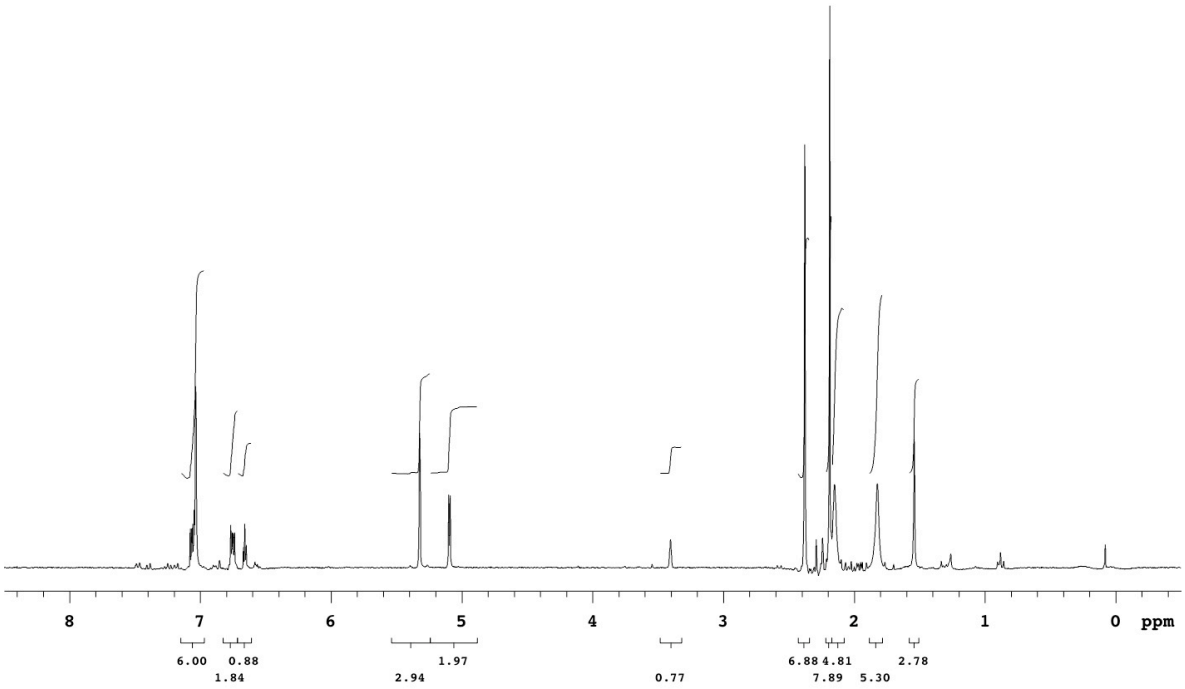
Oxime cyclopalladate **15b**:



Indenylpalladium Complex **16a**:



Indenylpalladium Complex **16b**:



VI. X-ray Structure Determination for 8ai

Crystallographic data for **8a*i*** have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 655348.

Figure S1. ORTEP Diagram for **8a*i***

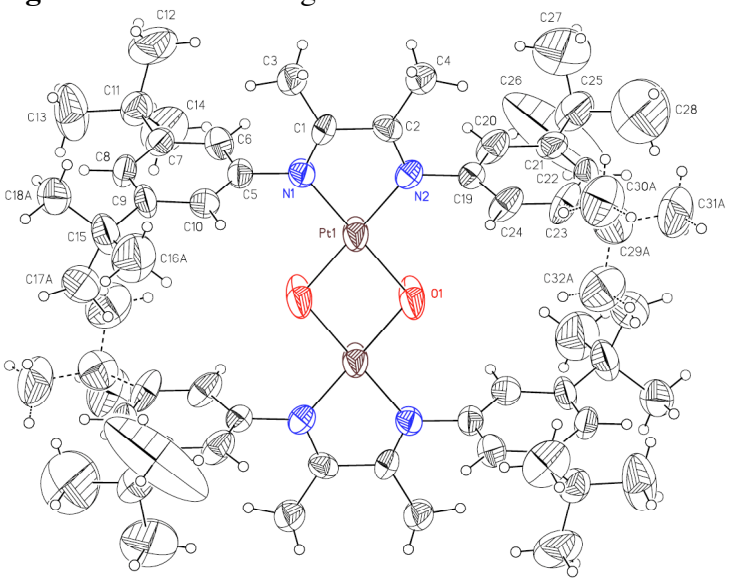


Table S6. Bond lengths [Å] for **8a*i***

Atom-Atom	Distance (Å)	Atom-Atom	Distance (Å)
Pt(1)-N(2)	1.940(5)	C(15)-C(16A)	1.505(7)
Pt(1)-N(1)	1.967(5)	C(15)-C(18B)	1.526(8)
Pt(1)-O(1)	2.045(5)	C(15)-C(17B)	1.533(7)
Pt(1)-O(1)#1	2.052(5)	C(15)-C(18A)	1.537(7)
Pt(1)-Pt(1)#1	3.1530(6)	C(15)-C(17A)	1.568(7)
O(1)-Pt(1)#1	2.052(5)	C(15)-C(16B)	1.566(8)
N(1)-C(1)	1.275(7)	C(19)-C(24)	1.338(7)
N(1)-C(5)	1.441(7)	C(19)-C(20)	1.366(8)
N(2)-C(2)	1.314(7)	C(20)-C(21)	1.386(8)
N(2)-C(19)	1.471(7)	C(21)-C(22)	1.328(9)
C(1)-C(2)	1.470(8)	C(21)-C(25)	1.557(10)
C(1)-C(3)	1.505(8)	C(22)-C(23)	1.369(9)
C(2)-C(4)	1.493(8)	C(23)-C(24)	1.384(9)
C(5)-C(6)	1.376(8)	C(23)-C(29A)	1.569(15)
C(5)-C(10)	1.381(8)	C(23)-C(29B)	1.636(15)
C(6)-C(7)	1.390(8)	C(25)-C(26)	1.414(14)
C(7)-C(8)	1.390(8)	C(25)-C(27)	1.445(13)
C(7)-C(11)	1.511(9)	C(25)-C(28)	1.533(14)
C(8)-C(9)	1.377(8)	C(29A)-C(30A)	1.527(8)
C(9)-C(10)	1.386(8)	C(29A)-C(31A)	1.529(8)
C(9)-C(15)	1.524(9)	C(29A)-C(32A)	1.537(8)
C(11)-C(14)	1.508(9)	C(29B)-C(32B)	1.521(8)
C(11)-C(13)	1.517(9)	C(29B)-C(30B)	1.528(8)
C(11)-C(12)	1.535(10)	C(29B)-C(31B)	1.531(8)

Table S7. Bond angles [°] for **8a*i***

Atom-Atom-Atom	Angle (°)	Atom-Atom-Atom	Angle (°)
N(2)-Pt(1)-N(1)	79.1(2)	C(18B)-C(15)-C(17A)	70.0(7)
N(2)-Pt(1)-O(1)	100.60(19)	C(17B)-C(15)-C(17A)	50.5(6)
N(1)-Pt(1)-O(1)	178.1(3)	C(18A)-C(15)-C(17A)	106.3(5)
N(2)-Pt(1)-O(1)#1	179.9(3)	C(16A)-C(15)-C(16B)	46.7(6)
N(1)-Pt(1)-O(1)#1	100.9(2)	C(18B)-C(15)-C(16B)	106.9(6)
O(1)-Pt(1)-O(1)#1	79.4(2)	C(17B)-C(15)-C(16B)	106.4(6)
N(2)-Pt(1)-Pt(1)#1	140.37(14)	C(18A)-C(15)-C(16B)	73.7(7)
N(1)-Pt(1)-Pt(1)#1	140.49(15)	C(17A)-C(15)-C(16B)	148.3(9)
O(1)-Pt(1)-Pt(1)#1	39.77(13)	C(16A)-C(15)-C(9)	116.0(8)
O(1)#1-Pt(1)-Pt(1)#1	39.61(13)	C(18B)-C(15)-C(9)	114.7(9)
Pt(1)-O(1)-Pt(1)#1	100.6(2)	C(17B)-C(15)-C(9)	114.0(8)
C(1)-N(1)-C(5)	117.9(5)	C(18A)-C(15)-C(9)	109.1(7)
C(1)-N(1)-Pt(1)	116.3(4)	C(17A)-C(15)-C(9)	105.6(7)
C(5)-N(1)-Pt(1)	125.8(4)	C(16B)-C(15)-C(9)	104.1(8)
C(2)-N(2)-C(19)	117.6(5)	C(24)-C(19)-C(20)	122.1(6)
C(2)-N(2)-Pt(1)	117.5(4)	C(24)-C(19)-N(2)	119.5(6)
C(19)-N(2)-Pt(1)	124.8(4)	C(20)-C(19)-N(2)	118.4(6)
N(1)-C(1)-C(2)	114.7(5)	C(19)-C(20)-C(21)	118.9(6)
N(1)-C(1)-C(3)	126.6(6)	C(22)-C(21)-C(20)	118.9(6)
C(2)-C(1)-C(3)	118.6(6)	C(22)-C(21)-C(25)	123.8(7)
N(2)-C(2)-C(1)	111.7(5)	C(20)-C(21)-C(25)	117.2(7)
N(2)-C(2)-C(4)	125.8(6)	C(21)-C(22)-C(23)	122.3(6)
C(1)-C(2)-C(4)	122.4(6)	C(22)-C(23)-C(24)	118.8(6)
C(6)-C(5)-C(10)	122.3(6)	C(22)-C(23)-C(29A)	114.0(8)
C(6)-C(5)-N(1)	117.2(6)	C(24)-C(23)-C(29A)	126.4(8)
C(10)-C(5)-N(1)	120.5(6)	C(22)-C(23)-C(29B)	128.8(7)
C(5)-C(6)-C(7)	119.7(6)	C(24)-C(23)-C(29B)	110.8(8)
C(6)-C(7)-C(8)	117.4(6)	C(29A)-C(23)-C(29B)	25.9(6)
C(6)-C(7)-C(11)	119.9(6)	C(19)-C(24)-C(23)	118.8(6)
C(8)-C(7)-C(11)	122.6(6)	C(26)-C(25)-C(27)	115.8(12)
C(7)-C(8)-C(9)	123.1(6)	C(26)-C(25)-C(28)	110.0(12)
C(8)-C(9)-C(10)	118.7(6)	C(27)-C(25)-C(28)	101.5(10)
C(8)-C(9)-C(15)	122.0(6)	C(26)-C(25)-C(21)	111.8(9)
C(10)-C(9)-C(15)	119.2(6)	C(27)-C(25)-C(21)	108.8(8)
C(5)-C(10)-C(9)	118.7(6)	C(28)-C(25)-C(21)	108.2(9)
C(7)-C(11)-C(14)	109.1(6)	C(30A)-C(29A)-C(31A)	109.4(7)
C(7)-C(11)-C(13)	114.4(6)	C(30A)-C(29A)-C(32A)	108.9(7)
C(14)-C(11)-C(13)	108.6(7)	C(31A)-C(29A)-C(32A)	108.9(7)
C(7)-C(11)-C(12)	108.4(6)	C(30A)-C(29A)-C(23)	111.3(9)
C(14)-C(11)-C(12)	108.1(7)	C(31A)-C(29A)-C(23)	116.7(10)
C(13)-C(11)-C(12)	108.1(7)	C(32A)-C(29A)-C(23)	101.1(10)
C(16A)-C(15)-C(18B)	127.2(11)	C(32B)-C(29B)-C(30B)	110.4(7)
C(16A)-C(15)-C(17B)	60.2(6)	C(32B)-C(29B)-C(31B)	109.8(7)
C(18B)-C(15)-C(17B)	109.9(6)	C(30B)-C(29B)-C(31B)	109.2(7)
C(16A)-C(15)-C(18A)	110.6(6)	C(32B)-C(29B)-C(23)	116.9(10)
C(18B)-C(15)-C(18A)	36.6(7)	C(30B)-C(29B)-C(23)	98.7(13)
C(17B)-C(15)-C(18A)	135.1(9)	C(31B)-C(29B)-C(23)	111.2(10)
C(16A)-C(15)-C(17A)	108.6(6)		

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+1,-z+1

VII. X-ray Structure Determination for 12

Crystallographic data for **12** have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 665648.

Figure S1. ORTEP Diagram for **12**

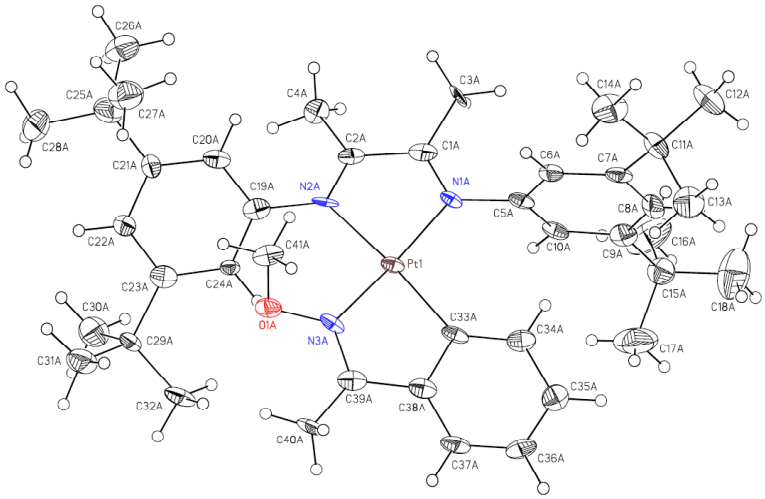


Table S8. Bond lengths [Å] for **12**

Atom-Atom	Distance (Å)	Atom-Atom	Distance (Å)
Pt(1)-N(3A)	2.014(8)	Pt(2)-N(3B)	2.003(8)
Pt(1)-C(33A)	2.036(10)	Pt(2)-N(1B)	2.036(8)
Pt(1)-N(1A)	2.042(7)	Pt(2)-C(33B)	2.047(10)
Pt(1)-N(2A)	2.115(8)	Pt(2)-N(2B)	2.117(8)
O(1A)-N(3A)	1.380(10)	O(1B)-N(3B)	1.382(10)
O(1A)-C(41A)	1.424(11)	O(1B)-C(41B)	1.442(11)
N(1A)-C(1A)	1.292(11)	N(1B)-C(1B)	1.315(11)
N(1A)-C(5A)	1.449(12)	N(1B)-C(5B)	1.437(13)
N(2A)-C(2A)	1.305(12)	N(2B)-C(2B)	1.297(12)
N(2A)-C(19A)	1.425(13)	N(2B)-C(19B)	1.427(12)
N(3A)-C(39A)	1.311(12)	N(3B)-C(39B)	1.321(12)
C(1A)-C(3A)	1.485(13)	C(1B)-C(3B)	1.506(13)
C(1A)-C(2A)	1.484(14)	C(1B)-C(2B)	1.480(14)
C(2A)-C(4A)	1.483(12)	C(2B)-C(4B)	1.508(13)
C(5A)-C(6A)	1.376(13)	C(5B)-C(6B)	1.392(13)
C(5A)-C(10A)	1.384(13)	C(5B)-C(10B)	1.401(12)
C(6A)-C(7A)	1.401(14)	C(6B)-C(7B)	1.372(14)
C(7A)-C(8A)	1.389(14)	C(7B)-C(8B)	1.433(13)
C(7A)-C(11A)	1.535(13)	C(7B)-C(11B)	1.533(14)
C(8A)-C(9A)	1.407(13)	C(8B)-C(9B)	1.376(13)
C(9A)-C(10A)	1.407(14)	C(9B)-C(10B)	1.382(14)
C(9A)-C(15A)	1.531(14)	C(9B)-C(15B)	1.543(13)
C(11A)-C(14A)	1.570(15)	C(11B)-C(13B)	1.502(15)
C(11A)-C(12A)	1.532(15)	C(11B)-C(14B)	1.559(16)
C(11A)-C(13A)	1.574(15)	C(11B)-C(12B)	1.545(15)
C(15A)-C(18A)	1.522(16)	C(15B)-C(18B)	1.558(15)
C(15A)-C(16A)	1.540(15)	C(15B)-C(16B)	1.542(17)

C(15A)-C(17A)	1.526(16)	C(15B)-C(17B)	1.568(16)
C(19A)-C(20A)	1.387(13)	C(19B)-C(20B)	1.362(13)
C(19A)-C(24A)	1.395(12)	C(19B)-C(24B)	1.404(13)
C(20A)-C(21A)	1.357(14)	C(20B)-C(21B)	1.412(14)
C(21A)-C(22A)	1.408(13)	C(21B)-C(22B)	1.395(14)
C(21A)-C(25A)	1.545(15)	C(21B)-C(25B)	1.544(15)
C(22A)-C(23A)	1.385(13)	C(22B)-C(23B)	1.389(13)
C(23A)-C(24A)	1.380(13)	C(23B)-C(24B)	1.417(14)
C(23A)-C(29A)	1.562(13)	C(23B)-C(29B)	1.525(12)
C(25A)-C(28A)	1.528(16)	C(25B)-C(27B)	1.37(2)
C(25A)-C(27A)	1.502(16)	C(25B)-C(28B)	1.469(18)
C(25A)-C(26A)	1.574(16)	C(25B)-C(26B)	1.62(2)
C(29A)-C(32A)	1.532(14)	C(29B)-C(32B)	1.530(14)
C(29A)-C(30A)	1.548(14)	C(29B)-C(31B)	1.542(14)
C(29A)-C(31A)	1.534(15)	C(29B)-C(30B)	1.565(14)
C(33A)-C(34A)	1.378(14)	C(33B)-C(34B)	1.369(14)
C(33A)-C(38A)	1.405(13)	C(33B)-C(38B)	1.411(14)
C(34A)-C(35A)	1.413(14)	C(34B)-C(35B)	1.411(14)
C(35A)-C(36A)	1.377(14)	C(35B)-C(36B)	1.371(15)
C(36A)-C(37A)	1.368(15)	C(36B)-C(37B)	1.365(15)
C(37A)-C(38A)	1.403(13)	C(37B)-C(38B)	1.403(13)
C(38A)-C(39A)	1.487(14)	C(38B)-C(39B)	1.465(14)
C(39A)-C(40A)	1.448(14)	C(39B)-C(40B)	1.469(14)

Table S9. Bond angles [°] for **12**

Atom-Atom-Atom	Angle (°)	Atom-Atom-Atom	Angle (°)
N(3A)-Pt(1)-C(33A)	78.9(4)	N(3B)-Pt(2)-N(1B)	176.0(3)
N(3A)-Pt(1)-N(1A)	175.4(3)	N(3B)-Pt(2)-C(33B)	79.4(4)
C(33A)-Pt(1)-N(1A)	103.7(3)	N(1B)-Pt(2)-C(33B)	102.7(4)
N(3A)-Pt(1)-N(2A)	100.6(3)	N(3B)-Pt(2)-N(2B)	100.6(3)
C(33A)-Pt(1)-N(2A)	171.2(3)	N(1B)-Pt(2)-N(2B)	77.9(3)
N(1A)-Pt(1)-N(2A)	77.4(3)	C(33B)-Pt(2)-N(2B)	170.8(3)
N(3A)-O(1A)-C(41A)	107.8(7)	N(3B)-O(1B)-C(41B)	107.3(7)
C(1A)-N(1A)-C(5A)	119.1(8)	C(1B)-N(1B)-C(5B)	118.8(8)
C(1A)-N(1A)-Pt(1)	116.7(7)	C(1B)-N(1B)-Pt(2)	116.1(7)
C(5A)-N(1A)-Pt(1)	124.0(6)	C(5B)-N(1B)-Pt(2)	124.9(6)
C(2A)-N(2A)-C(19A)	119.1(8)	C(2B)-N(2B)-C(19B)	119.5(8)
C(2A)-N(2A)-Pt(1)	114.6(7)	C(2B)-N(2B)-Pt(2)	114.4(7)
C(19A)-N(2A)-Pt(1)	126.1(6)	C(19B)-N(2B)-Pt(2)	126.1(6)
C(39A)-N(3A)-O(1A)	116.3(8)	C(39B)-N(3B)-O(1B)	116.8(8)
C(39A)-N(3A)-Pt(1)	120.3(7)	C(39B)-N(3B)-Pt(2)	119.1(7)
O(1A)-N(3A)-Pt(1)	123.3(5)	O(1B)-N(3B)-Pt(2)	123.9(6)
N(1A)-C(1A)-C(3A)	123.5(9)	N(1B)-C(1B)-C(3B)	123.9(9)
N(1A)-C(1A)-C(2A)	116.1(8)	N(1B)-C(1B)-C(2B)	115.8(9)
C(3A)-C(1A)-C(2A)	120.4(8)	C(3B)-C(1B)-C(2B)	120.3(8)
N(2A)-C(2A)-C(4A)	126.4(9)	N(2B)-C(2B)-C(1B)	115.2(8)
N(2A)-C(2A)-C(1A)	114.5(8)	N(2B)-C(2B)-C(4B)	126.7(9)
C(4A)-C(2A)-C(1A)	119.1(9)	C(1B)-C(2B)-C(4B)	118.0(9)
C(6A)-C(5A)-C(10A)	123.0(10)	C(6B)-C(5B)-C(10B)	122.8(10)
C(6A)-C(5A)-N(1A)	118.2(9)	C(6B)-C(5B)-N(1B)	117.8(8)
C(10A)-C(5A)-N(1A)	118.8(9)	C(10B)-C(5B)-N(1B)	119.3(9)
C(5A)-C(6A)-C(7A)	118.9(9)	C(7B)-C(6B)-C(5B)	119.1(9)
C(8A)-C(7A)-C(6A)	118.4(9)	C(6B)-C(7B)-C(8B)	118.1(9)

C(8A)-C(7A)-C(11A)	118.9(9)	C(6B)-C(7B)-C(11B)	120.1(8)
C(6A)-C(7A)-C(11A)	122.7(9)	C(8B)-C(7B)-C(11B)	121.9(9)
C(7A)-C(8A)-C(9A)	123.3(10)	C(9B)-C(8B)-C(7B)	122.0(10)
C(8A)-C(9A)-C(10A)	116.9(9)	C(8B)-C(9B)-C(10B)	119.7(9)
C(8A)-C(9A)-C(15A)	123.3(10)	C(8B)-C(9B)-C(15B)	118.7(9)
C(10A)-C(9A)-C(15A)	119.9(9)	C(10B)-C(9B)-C(15B)	121.6(9)
C(5A)-C(10A)-C(9A)	119.5(9)	C(9B)-C(10B)-C(5B)	118.2(9)
C(7A)-C(11A)-C(14A)	111.4(9)	C(13B)-C(11B)-C(7B)	113.9(9)
C(7A)-C(11A)-C(12A)	110.6(9)	C(13B)-C(11B)-C(14B)	108.2(9)
C(14A)-C(11A)-C(12A)	109.6(9)	C(7B)-C(11B)-C(14B)	106.8(9)
C(7A)-C(11A)-C(13A)	109.1(8)	C(13B)-C(11B)-C(12B)	110.0(10)
C(14A)-C(11A)-C(13A)	107.0(9)	C(7B)-C(11B)-C(12B)	108.9(8)
C(12A)-C(11A)-C(13A)	109.1(9)	C(14B)-C(11B)-C(12B)	108.9(9)
C(18A)-C(15A)-C(16A)	109.8(11)	C(18B)-C(15B)-C(9B)	109.5(8)
C(18A)-C(15A)-C(9A)	112.9(9)	C(18B)-C(15B)-C(16B)	109.6(10)
C(16A)-C(15A)-C(9A)	108.2(8)	C(9B)-C(15B)-C(16B)	108.9(9)
C(18A)-C(15A)-C(17A)	108.6(11)	C(18B)-C(15B)-C(17B)	107.8(9)
C(16A)-C(15A)-C(17A)	108.3(11)	C(9B)-C(15B)-C(17B)	111.6(9)
C(9A)-C(15A)-C(17A)	108.9(10)	C(16B)-C(15B)-C(17B)	109.4(9)
C(20A)-C(19A)-C(24A)	120.4(10)	C(20B)-C(19B)-C(24B)	121.8(9)
C(20A)-C(19A)-N(2A)	121.3(9)	C(20B)-C(19B)-N(2B)	120.7(9)
C(24A)-C(19A)-N(2A)	118.3(8)	C(24B)-C(19B)-N(2B)	117.5(9)
C(21A)-C(20A)-C(19A)	120.9(9)	C(19B)-C(20B)-C(21B)	120.2(9)
C(20A)-C(21A)-C(22A)	118.6(9)	C(22B)-C(21B)-C(20B)	117.9(9)
C(20A)-C(21A)-C(25A)	119.3(9)	C(22B)-C(21B)-C(25B)	122.0(10)
C(22A)-C(21A)-C(25A)	122.1(9)	C(20B)-C(21B)-C(25B)	120.0(9)
C(23A)-C(22A)-C(21A)	121.4(10)	C(23B)-C(22B)-C(21B)	122.8(10)
C(22A)-C(23A)-C(24A)	119.0(9)	C(24B)-C(23B)-C(22B)	118.0(9)
C(22A)-C(23A)-C(29A)	118.2(9)	C(24B)-C(23B)-C(29B)	121.0(8)
C(24A)-C(23A)-C(29A)	122.8(9)	C(22B)-C(23B)-C(29B)	121.0(9)
C(23A)-C(24A)-C(19A)	119.6(9)	C(23B)-C(24B)-C(19B)	119.1(9)
C(28A)-C(25A)-C(27A)	109.8(11)	C(27B)-C(25B)-C(28B)	115.5(18)
C(28A)-C(25A)-C(21A)	112.5(9)	C(27B)-C(25B)-C(21B)	113.1(11)
C(27A)-C(25A)-C(21A)	110.3(10)	C(28B)-C(25B)-C(21B)	108.9(10)
C(28A)-C(25A)-C(26A)	107.3(11)	C(27B)-C(25B)-C(26B)	109.2(19)
C(27A)-C(25A)-C(26A)	109.7(9)	C(28B)-C(25B)-C(26B)	102.4(12)
C(21A)-C(25A)-C(26A)	107.2(9)	C(21B)-C(25B)-C(26B)	106.9(11)
C(32A)-C(29A)-C(30A)	109.3(9)	C(32B)-C(29B)-C(31B)	107.6(8)
C(32A)-C(29A)-C(31A)	108.7(8)	C(32B)-C(29B)-C(23B)	113.3(8)
C(30A)-C(29A)-C(31A)	109.4(9)	C(31B)-C(29B)-C(23B)	109.3(8)
C(32A)-C(29A)-C(23A)	111.5(8)	C(32B)-C(29B)-C(30B)	108.4(8)
C(30A)-C(29A)-C(23A)	109.4(8)	C(31B)-C(29B)-C(30B)	108.9(9)
C(31A)-C(29A)-C(23A)	108.6(8)	C(23B)-C(29B)-C(30B)	109.2(8)
C(34A)-C(33A)-C(38A)	116.1(9)	C(34B)-C(33B)-C(38B)	116.8(9)
C(34A)-C(33A)-Pt(1)	131.1(7)	C(34B)-C(33B)-Pt(2)	131.5(8)
C(38A)-C(33A)-Pt(1)	112.2(7)	C(38B)-C(33B)-Pt(2)	111.2(7)
C(33A)-C(34A)-C(35A)	122.6(10)	C(33B)-C(34B)-C(35B)	121.7(10)
C(36A)-C(35A)-C(34A)	119.1(10)	C(36B)-C(35B)-C(34B)	120.1(10)
C(37A)-C(36A)-C(35A)	120.6(10)	C(35B)-C(36B)-C(37B)	120.0(10)
C(36A)-C(37A)-C(38A)	119.4(10)	C(36B)-C(37B)-C(38B)	119.7(10)
C(37A)-C(38A)-C(33A)	122.2(10)	C(37B)-C(38B)-C(33B)	121.6(10)
C(37A)-C(38A)-C(39A)	121.4(9)	C(37B)-C(38B)-C(39B)	121.7(9)
C(33A)-C(38A)-C(39A)	116.3(9)	C(33B)-C(38B)-C(39B)	116.4(9)

N(3A)-C(39A)-C(40A)	124.1(10)	N(3B)-C(39B)-C(38B)	111.9(9)
N(3A)-C(39A)-C(38A)	110.6(9)	N(3B)-C(39B)-C(40B)	123.7(10)
C(40A)-C(39A)-C(38A)	125.2(9)	C(38B)-C(39B)-C(40B)	124.3(9)

References

1, Prepared according to a known procedure: Wong-Foy, A. G.; Henling, L. M.; Day, M.; Labinger, J. A.; Bercaw, J. E. *J. Mol. Cat. A: Chem*. **2002**, *189*, 3-16.

2, Zeise's salt; commercially available through Aldrich and Strem and used as received.

3, Zhong, H. A.; Labinger, J. A.; Bercaw. J. E. *J. Am. Chem. Soc*. **2002**, *124*, 1378-1399.

4, Prepared according to a known procedure: S. Kannan, A. J. James, P. R. Sharp. *Polyhedron* **2000**, *19*, 155-163.

5, This solid was identified by NMR as a mixture of the dimer **8a*i*** and divalent salt **8a*ii***. Further purification (as described) converts these materials entirely to **8a*i***.

6, Driver, T. G.; Williams, T. J. Labinger, J. A.; Bercaw, J. E. *Organometallics* **2007**, *26*, 294-301, compound **15a**.

7, *ibid*, compound **14a**.

8, Prepared according to Beak, O.; Basha, A.; Kokko, B.; Loo, D. *J. Am. Chem. Soc*. **1986**, *108*, 6016-6023.

9, See Driver, T. G.; Labinger, J. A.; Bercaw, J. E. *Organometallics* **2005**, *24*, 3644-3654 (compound **9c**).

10, See: Laidler, K. J. *Chemical Kinetics*, 3rd ed.; Harper & Row: New York, 1987.

11, See Trost, B. M.; Metzner, P. J. *J. Am. Chem. Soc.* **1980**, *102*, 3572-3577.